การเตรียมและการปรับปรุงสมบัติของฟิล์มหด 3 ชั้น

ที่ได้จากพอลิเอทิลีนความหนาแน่นต่ำที่แปรใช้ใหม่

นางสาวโอมาตยา มนตรีกุล

PREPARATION AND PROPERTY IMPROVEMENT OF THREE LAYERED SHRINK FILM

BASED ON RECYCLED LOW DENSITY POLYETHYLENE

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A Dissertation Submitted in Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy Program in Materials Science

Department of Materials Science

Faculty of Science

Chulalongkorn University

Academic year 2009

Thesis Title	PREPARATION AND PROPERTY IMPROVEMENT OF THREE LAYERED SHRINK FILM BASED ON RECYCLED LOW DENSITY POLYETHYLENE
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โอมาตยา มนตรีกุล : การเตรียมและการปรับปรุงสมบัติของฟิล์มหด 3 ชั้นที่ได้จากพอลิเอทิลีนความหนาแน่นต่ำที่แปรใช้ใหม่ (PREPARATION AND PROPERTY IMPROVEMENT OF THREE LAYERED SHRINK FILM BASED ON RECYCLED LOW DENSITY POLYETHYLENE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. วิมลวรรณ พิมพ์พันธุ์, 158 หน้า.

ฟิล์มหด 3 ชั้นที่ได้จากพอลิเอทิลีนความหนาแน่นต่ำที่แปรใช้ใหม่ (re-LDPE) สามารถเตรียมได้จากการเป่าฟิล์มแบบร่วม โดยชั้นนอกประกอบด้วยพอลิเอทิลีนความหนาแน่นต่ำบริสุทธิ์ (LDPE) ส่วนชั้นกลางเป็นพอลิเมอร์ผสมระหว่าง LDPE กับ re-LDPE ที่อัตราส่วนโดยน้ำหนักเป็น 100:0, 85:15, 70:30, 55:45, 40:60 และ 0:100 จากการทดสอบสมบัติเชิงกลและการวิเคราะห์ทางความร้อนพบว่า ฟิล์มที่เตรียมจากพอลิเมอร์ผสมและที่ใช้ re-LDPE 100 เปอร์เซ็นต์โดยน้ำหนักมีสมบัติเชิงกลและพฤติกรรมทางความร้อนดีกว่าฟิล์มที่มีแต่ LDPE เพียงอย่างเดียว

สมบัติเชิงกล ซึ่งรวมถึงสมบัติด้านแรงดึง แรงยึดติด และความสามารถในการหดของฟิล์ม LDPE/re-LDPE/LDPE สามารถปรับปรุงได้โดยการนำพอลิเอทิลีนความหนาแน่นปานกลาง (MDPE) มาผสมในชั้นกลาง และพอลิเอทิลีนความหนาแน่นต่ำเชิงเส้น (LLDPE) มาผสมในชั้นนอก จากการทดลองพบว่า การใช้ MDPE 30 เปอร์เซ็นต์โดยน้ำหนัก และ LLDPE 30 เปอร์เซ็นต์โดยน้ำหนัก ให้ฟิล์มที่มีแรงยึดติดสูงสุดและมีสมบัติด้านแรงดึงที่ดีกว่าฟิล์มที่มีแต่พอลิเอทิลีนความหนาแน่นต่ำบริสุทธิ์และที่แปรใช้ใหม่ นอกจากนี้ ฟิล์มดังกล่าวยังมีความสามารถในการหดอยู่ในระดับมาตรฐานทางการค้าสำหรับการประยุกต์ด้านฟิล์มหดอีกด้วย

อีกแนวทางหนึ่งที่สามารถนำมาใช้ปรับปรุงสมบัติเชิงกลของฟิล์ม LDPE/re-LDPE/LDPE ได้ คือ การเติมแคลเซียมคาร์บอเนตลงในชั้นกลาง ผลการวิเคราะห์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงให้เห็นถึงการกระจายตัวที่ดีของแคลเซียมคาร์บอเนตในเมทริกซ์ re-LDPE ซึ่งส่งผลให้ฟิล์มที่ได้มีสมบัติด้านแรงดึงที่ดีกว่า อย่างไรก็ตาม การเติมแคลเซียมคาร์บอเนตที่มากเกินไป ทำให้สมบัติทางแสงและแรงยึดติดลดลงแต่ความสามารถในการหดเพิ่มขึ้นปริมาณของแคลเซียมคาร์บอเนตที่เหมาะสมที่สุด คือ 7.5 เปอร์เซ็นต์โดยน้ำหนัก

ภาควิชา   วัสดุศาสตร์   ลายมือชื่อนิสิต
สาขาวิชา   วัสดุศาสตร์   ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา   2552

4873871123 : MAJOR MATERIALS SCIENCE

KEYWORDS : LOW DENSITY POLYETHYLENE / SHRINK FILM / RECYCLE / CO-EXTRUSION / THREE LAYERED FILM

OMATTAYA MONTRIKUL : PREPARATION AND PROPERTY IMPROVEMENT OF THREE LAYERED SHRINK FILM BASED ON RECYCLED LOW DENSITY POLYETHYLENE. THESIS ADVISOR : ASSOC. PROF. VIMOLVAN PIMPAN, Ph.D., 158 pp.

Three layered shrink films based on recycled low density polyethylene (re-LDPE) were prepared by blown film co-extrusion. The outer layers contained only virgin LDPE while the middle layer composed of the blends between LDPE and re-LDPE at weight ratios of 100:0, 85:15, 70:30, 55:45, 40:60 and 0:100. From mechanical tests and thermal analysis, it was found that all films prepared from polymer blends and from re-LDPE 100 wt% (LDPE/re-LDPE/LDPE film) exhibited better mechanical properties and thermal behaviors than the film containing only LDPE.

The mechanical properties including tensile properties, seal strength and shrink ability of LDPE/re-LDPE/LDPE film were improved by blending the middle layer with medium density polyethylene (MDPE) and the outer layer with linear low density polyethylene (LLDPE). It was found that using 30 wt% of MDPE and 30 wt% of LLDPE gave the film that had highest seal strength and better tensile properties than the film containing only LDPE and re-LDPE. In addition, this film also exhibited the shrink ability within the commercial standard for shrink film applications.

On the other hand, adding calcium carbonate ($CaCO_3$) into re-LDPE middle layer also improved mechanical properties of LDPE/re-LDPE/LDPE film. SEM analysis revealed the good dispersion of $CaCO_3$ in re-LDPE matrix resulting in better tensile properties. However, adding too much $CaCO_3$ decreased the optical property and seal strength but increased shrink ability. The suitable amount of $CaCO_3$ to be added was 7.5 wt%.

Department : _____Materials Science_____ Student's Signature _____

Field of Study : _____Materials Science_____ Advisor's Signature _____

Academic Year : ____2009_____

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1.1 General introduction

Shrink film is generally made from low density polyethylene (LDPE) by blown film extrusion in the forms of monolayer and multilayer. It is designed to over-wrap and tightly seal many varieties of products with different shapes and sizes both individual and multipack for protection during storage and transportation. Its main application is the packaging of beverage, dairy, pharmaceutical, food, cosmetic and chemical products. Due to its high consumption, the waste from LDPE shrink film is not only generated during the manufacturing process but also disposed after-use. Since LDPE is not biodegradable, the accumalation of its waste can cause environmental problem.

Thermo-mechanical recycling by reprocessing technique is the popular method for elimination of the plastic waste because it is technical and economical feasibility. However, this process can cause thermal degradation of the polymer molecules resulting in a decrease in mechanical and thermal properties of the recycled products when compared to those made of only virgin polymer. In addition, the deterioration of these properties increases with increasing the number of reprocessing cycle. To overcome these problems, some additives such as antioxidant, UV stabilizer, thermal resistant, impact modifier, inert filler and various polymers such as HDPE, LLDPE, PP and PET are widely used to mix or blend for improving these properties.

However, even adding the additives or blending with other polymers, it is found that a recycling of a plastic waste into a monolayered film by blown film extrusion, many defects such as melt fracture, scratch and burn spot can still occur in recycled plastic film. This is because the recycled polymer is in a direct contact with the heated die and barrel wall. As a result, thermal degradation can still occur. Therefore, three layered film consisting of a recycled polymer as the middle layer and a virgin polymer as the outer layers may be the solution to solve this problem. This type of film can be produced by

blown film co-extrusion. In this process, the achievement of the specific properties of a multilayered film depends on the characteristics and properties of the polymers of each layer.

1.2 The objectives of the thesis

Main objectives of this thesis are as follows:

a. to prepare three layered shrink films using recycled low density polyethylene (re-LDPE) as a middle layer.

b. to improve the mechanical properties of three layered shrink films based on re-LDPE by blending method.

c. to improve the mechanical properties of three layered shrink films based on re-LDPE by addition of calcium carbonate.

d. to study the effects of calcium carbonate and polymer blends on optical and thermal properties of the prepared three layered shrink films.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polyethylene

Polyethylene (PE) is a thermoplastic material particularly well suited for fabrication into many products due to its many excellent or good properties. More than 60% of packaging films such as heat shrink film are made from PE. Since PE molecule comprises only of carbon and hydrogen atoms aligning in alkane form as shown in Figure 2.1, it exhibits excellent water resistance and good chemical resistance. However, it is swollen in the presence of hydrocarbon and chlorinated solvents at room temperature. Besides being excellent electrical insulator, PE also has a good combination of melt flow behavior and mechanical properties such as impact strength, tensile strength and flexibility [1].

$$-(CH_2-CH_2)_n-$$
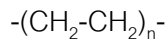
Figure 2.1 Chemical structure of polyethylene

PE is polymerized from ethylene monomer via several reactions. It can be characterized by average molecular weight as the function of melt flow index, the degree of crystallinity as the function of density, molecular weight distribution (MWD) or the degree and type of long chain branching. Generally, PE is classified according to its density into three types as low density polyethylene (LDPE) having density from 0.910 to 0.930 g/cm^3, medium density polyethylene (MDPE) having density from 0.920 to 0.940 g/cm^3 and high density polyethylene (HDPE) whose density is more than 0.940 g/cm^3, respectively [2].

2.1.1 Low density polyethylene (LDPE)

Low density polyethylene (LDPE) is synthesized by radical chain polymerization. Depending on polymerization conditions including temperature, pressure, ethylene concentration and reactor type, LDPE products having different molecular weight, molecular weight distribution (MWD) and extents of branching are obtained. For example, long-chain branching increases with increasing temperature and conversion but decreases with increasing pressure or using autoclave processes instead of tubular process results in PE having narrower MWD and higher long chain branching [1]. Long PE molecules have several branches along its backbones both short-chain branches (SCB) and long-chain branches (LCB) as shown in Figure 2.2. Long-chain branches improve melt strength and elasticity compared to SCB and increase the entanglement among the polymer molecules resulting in good bubble stability during the blown film process.

Long-chain branches   Short-chain branches

Figure 2.2 PE chains containing different type of branch

LDPE molecules form the spherulites in solid state where the polymer chains fold into the crystalline regions whereas the amorphous regions are formed under the disrupted folding. The size distribution of the spherulites has influenced on the density of the polymer. As the density increases, the mechanical properties such as stiffness and hardness, melting and heat seal temperature increase but impact property decreases.

LDPE has several molecular weights both low and high. Commercial LDPE has number-average molecular weight in the range of 20,000-100,000 with $\overline{X}_w / \overline{X}_n$ in the range of 3-20. LDPE has glass transition temperature (T_g) of about -120 ^{0}C and melting temperature (T_m) of 105-115 ^{0}C. Processing of LDPE is easier than other PE grades

because it can be melted at lower temperature and does not require much extruder motor power. LDPE film grades have moderately high viscosity. They have wide range of chain branching resulting in a broad processing window and high melt strength leading to a stable bubble that can be run with a low frost-line height and high output. The elastic nature of LDPE can contribute to the production of the films with high toughness, high impact resistant, high tensile strength and good seal ability. It is designed to cover and protect many products or maintain the pallets during storage and transportation. It can also be used for agriculture films, mulch films, greenhouse coverings and tubing liner films [1, 2].

2.1.2 High density polyethylene (HDPE)

High density polyethylene (HDPE) is synthesized by coordination polymerization using traditional Ziegler-Natta catalyst and Phillips-type initiator. Its structure as shown in Figure 2.3 is almost linear. Its degree of branching is 0.5-3 methyl groups per 500 monomer units compared to LDPE which has the degree of branching of 15-30 methyl groups per 500 monomer units. Therefore, HDPE and LDPE are sometimes called linear and branched PEs, respectively. Due to this characteristic, HDPE exhibits higher %crystallinity, density and melting temperature than LDPE. While the former exhibits these three values of 70-90%, 0.94-0.96 $g.mL^{-1}$ and 133-138 ^{o}C, those of the latter are 40-60%, 0.91-0.93 $g.mL^{-1}$ and 105-115 ^{o}C, respectively [1].

Figure 2.3 Molecular structure of HDPE

In addition, HDPE has higher tensile strength, higher stiffness, better chemical resistance, higher upper-use temperature and better resistance to stress cracking but

higher tendency to wrinkle, lower impact strength and more difficult to process than LDPE. HDPE generally has number-average molecular weight in the range of 50,000-250,000. Higher molecular weight results in higher tensile strength, elongation, low-temperature impact resistance, and better stress crack resistance, although processing is more expensive because of its increased melt viscosity. HDPE film provides many advantages especially where high stiffness products are required such as bottom bag, standing pouch, moisture-barrier packaging.

Biaxial orientation of HDPE film during the blown film process can be generated in both machine direction (MD) and transverse direction (TD) by controlling the bubble geometry. As the molten polymer flows through the extruder, it has a random orientation through the spirals die and exits the die lip which results in developing a gradient velocity and causes the molecules to orient in MD. As HDPE melt exits the die, it needs a relatively long frost-line height to allow the molecules to relax and improve melt strength [2-3]. Blow up ratio (BUR) is the ratio of the final film bubble diameter to the die diameter. At high blow up ratio (BUR), the resulting film physically stretches the polymer in TD and assists in optimizing the molecular orientation of the film in both MD and TD. HDPE bubble geometry is quite different than conventional LDPE because it is usually run with a high frost-line height on the order of eight to ten times the die diameter because it has a lower melt strength as shown in Figure 2.4.

$$BUR = \frac{Bubble\ diameter\ (D)}{Die\ diameter\ (d)}$$
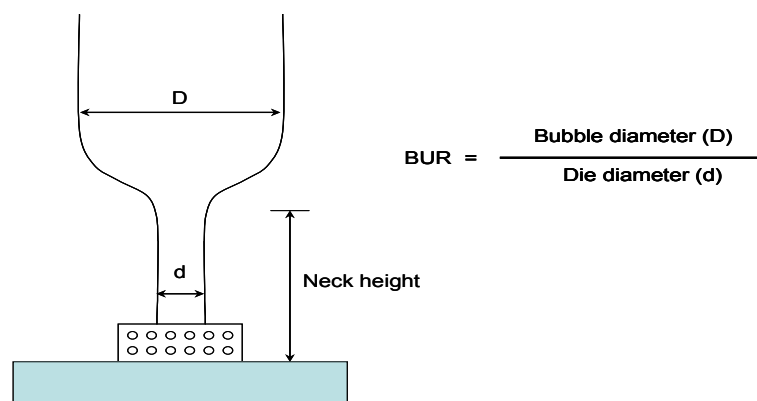
Figure 2.4 HDPE bubble geometry with high frost-line height

2.1.3 Medium density polyethylene (MDPE)

Medium density polyethylene (MDPE) is synthesized by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. It has a density range of 0.920 - 0.940 g/cm^3 and higher degree of branching than HDPE as shown in Figure 2.5. MDPE has good shock and drop resistance properties. Compared to HDPE, MDPE has less notch sensitivity and better stress cracking resistance. MDPE is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures [4-5].

Figure 2.5 Molecular structure of MDPE

2.1.4 Linear low density polyethylene (LLDPE)

Linear low density polyethylene (LLDPE) is synthesized by coordination copolymerization of ethylene with small amounts of an α-olefin such as 1-butene, 1-hexene, or 1-octene using a type of Ziegler-Natta (Z-N) catalyst [6]. Copolymerization with propene, 4-methyl-1-pentene, and cycloalkenes is also reported. By adjusting the comonomer content, the amount of short branches including ethyl, n-butyl, and n-hexyl branches can be controlled [1]. The obtained structure as shown in Figure 2.6 affects the degree of crystallinity and the density of the polymer. It has the density in a range of 0.88-0.93 g/cm^3. The mechanical properties of LLDPE are the combination of those of HDPE and LDPE properties. For example, it has higher tensile strength and toughness than LDPE but lower stiffness than HDPE.

Figure 2.6 Molecular structure of LLDPE

A good characteristic of LLDPE is a narrow molecular weight distribution compared to LDPE resulting in the significant improvement of tear strength, puncture resistance, tensile strength and stiffness properties. Another key difference between LLDPE and LDPE is the melt strength. In film fabrication, melt deformation occurs outside the die as the film is drawn down to the desired thickness. During the melt extension, the extensional viscosity of LDPE increases as the deformation rate increases due to strain hardening. This stress increasing at high strain rates is quite different for LLDPE where little strain hardening is observed. Thus the drawdown capability of LLDPE is very good. In the blown film process, strain hardening of the melt imparts bubble stability. The low stress buildup of LLDPE provides a melt that exhibits low melt strength when compare to LDPE. Thus, LLDPE has an inability to withstand the impingement of high velocity cooling air on the melt surface. This requires some modification in air ring design in blown film [2].

2.2 Blown film extrusion and extruder hardware systems

PE resins are widely used in a variety of plastic film applications both in the form of monolayer and multilayer films. Polymer chemistry and molecular structure are vital in establishing film properties. One of the most important processing method for plastic films is blown film extrusion. The bubble geometry resulting from processing conditions is also significant in order to control the molecular orientation, the crystal structure and the film properties. One significant characteristic of all PE grades is high value of specific heat. The specific heat is a measure of the energy required to raise a unit mass of material one degree in temperature. If a polymer has a high value of specific heat, this means that heat removal from the melt is relatively slow. PE has a specific heat

of approximately 2 kJ/kg.K compared to approximately 1 kJ/kg.K for most other polymers. This is a reason why the cooling towers for PE blown film are very high. It takes time to remove enough heat from the two layers passing through the nip rollers in order to prevent them from sticking together or blocking. The purpose of the extruder is to feed a die with a homogeneous material at constant temperature and pressure [4]. In blown film process, resin pellets are fed through a hopper into an extruder. The pellets are converted into a molten state by the frictional heat generated between the polymer, the screw and the barrel wall. Monolayer blown film extrusion uses only the single extruder system but co-extrusion is the process of feeding polymer pellets into two or more extruders through a single die [7]. The multilayer product is formed at the die and allows the product to have different properties on each side. Co-extrusion has potential to produce thinner layers than monolayer. The main reason for co-extruding film is to obtain a particular set of properties in the final film structure that depends on the contributions of multiple polymers [3]. The various layers often contribute the require properties such as high strength, low permeability (barrier) to oxygen and carbon dioxide for longer shelf life, printability, dual colors, heat seal property, high transparent films, greater puncture resistance, reduced tear propagation, anti blocking, slip properties and reducing cost [8-9].

The principal components of the blown film extruder hardware are hopper, grooved feed throat, screw and barrel, blown film dies, bubble geometry, bubble cooling, bubble stabilization, collapsing frames, haul-off, roller and winders that are classified by the order of material flows though the extrusion line, starting from the upstream component of the extruder to the roller winding.

2.2.1 Hopper

Hopper is the upstream component of blown film extruder associated with feeding solid material into the screw and barrel as shown in Figure 2.7. The solid materials have several forms such as pellet, powder, flake, and fluff. The consistent pellet geometry has a good effect to benefit for consistent feeding and film properties.

Normally, recycled polymer pellets are made of film waste scraps derived from the production process such as handle cutouts from a bag making machine or edge trimming from bubble tubing into a single lay flat film. They have at least two heat histories which leading to the degradation of polymer molecules and higher variation of the pellet geometry than virgin polymer pellets.

Figure 2.7 Hopper of a blown film extrusion machine

2.2.2 Grooved feed throat

The feed throat section of the extruder is located in the bottom hopper between the gear box and the barrel. The grooved feed throat as shown in Figure 2.8 is an important component used for increasing the output rate because it is designed to increase the friction between the polymer pellets and the surface of barrel which leads to an increase in the melt flow rate through the die. The solid conveyance rate strongly depends on two frictional interactions between the feed material with the barrel and the screw. However, grooved feed throat requires the efficient cooling system to prevent the possibility of overheating which results in damaged materials.
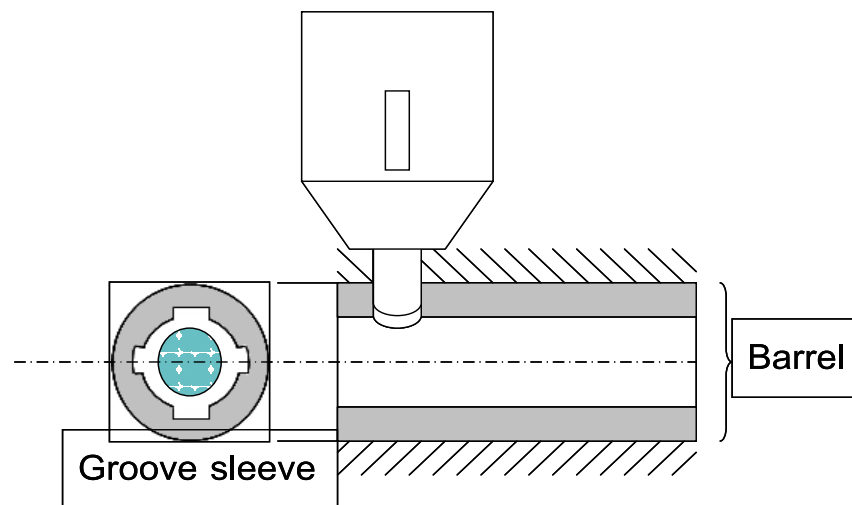
Figure 2.8 Drawing of the feed throat of an extruder

2.2.3 Screw and barrel

In the plastic industry, the screw and barrel system is the heart of extrusion process. The screw can be designed in many different forms such as single, twin or multi-screw configurations. A different screw designs may be desired for different processes such as a profile extrusion application, a blown film application and blow molding application. It has a very specific requirement that optimum for each process and application in order to improve higher throughput rates, better dispersion and a good mixing of raw materials. The optimum screw design also makes the polymer melt to be homogeneous and feeds the polymer through the die with constant temperature and pressure. Temperature or pressure fluctuations can lead to the variations in the final product. Generally, most screws have three primary sections including feed, transition or compression and metering sections. Channel depth or screw flight is generally largest and constant in the feed section, then continuously decreases along the transition section, is smallest and constant in the metering section. The primary function of the feed section is to forward the polymer pellets into the compression zone. In compression zone, the resin is melted by the heat generated from the friction occurring between the resin and the barrel wall. The melting rate gradually increases due to an increase in the friction between the melted polymer, the resin and the barrel

wall. At metering zone, the homogeneous melt is obtained. The screw geometry quantified by the compression ratio and the L/D ratio are the important characteristic that defines the efficiency of the extruder. For example, if the flight of the screw in the feed zone is deep while that in the metering zone is small, the compression pressure and the friction are high. As a result, the heat is very high and not suitable for the plastic that cannot tolerate high heat. Those two ratios can be calculated by the following equations.

Compression ratio = Feed channel depth / Metering channel depth

L/D ratio = Screw flight length / Screw diameter

Typical values of compression ratio ranging from 2:1 to 4:1 depending on the type of polymer and the bulk density of the feed material. The most commonly used of L/D ratio rang from 18:1 to 32:1 but some functions would require a longer screw for mixing and degassing [3]. The barrel is a hollow cylinder extending from the end of the feed throat to the tip of the screw. The entire inside surface of the barrel is coated by a very hard material such as tungsten-carbide alloy in order to extend the life of the barrel by reducing scratch. Temperature control zones are located by cast aluminum heaters along the barrel length but high temperature system may require ceramic heaters. Some extruded materials require vented barrels for removing unwanted gases.

2.2.4   Blown film die

Blown film die is generally located the die gap vertically upward. It is used to receive polymer melt from the extruder and transport into the die exit as a thin annular film. The high performance of melt quality obtained not only of the screw design but also of the suitable design of the extrusion die resulting in the smoothly melt flows, uniform of melt velocity and no flow lines. There are several types of blown film dies varying in cost, complexity and the application. The cross-sections of a

typical spiral mandrel die that are mostly used for producing monolayer films are shown in Figure 2.9. The spiral design is the most important feature in the die design and has the most influence on die performance and melt distribution. Both the knowledge of the polymer flow properties (rheology) and the geometry of the spiral distribution system have influence on a uniform flow of polymer and the film bubble.
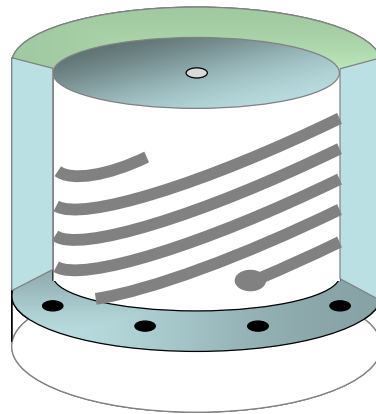
Figure 2.9 Drawing of a spiral mandrel die

Concentric and stack dies are two main types of co-extrusion blown film dies. Concentric dies are comprised of a series of hollow spiral mandrels where different polymers flow separately and at the die exit, the different polymers flow together into a single flow channel. Stack die separates the flow gaps between vertically stacked plates instead of nested mandrels. The advantage of a stack die is suitable for removal heating each layer when employing different materials with a wide range of melt temperatures. The die gap depends on several factors such as the material type, die diameter, blow-up ratio and film thickness. A smaller die gap is normally used for LDPE whereas larger die gaps are used for LLDPE and HDPE in order to reduce melt fracture on the polymer surface [2].

2.2.5 Bubble geometry

The bubble geometry has significant effects on the mechanical properties of the film including shrink ability, tensile strength, impact property in both machine and

transverse directions. Parameters controlling bubble geometry in the blown film processing are die diameter, die gap, frost-line height, stalk, film width, film thickness, bubble diameter (BD) and velocity of the film. Blow up ratio (BUR) and drawdown ratio (DDR) as defined by following equations are used to determined bubble geometry.

Blow up ratio (BUR) = Lay flat width / (die diameter x 1.57) or

Drawdown ratio (DDR) = velocity at haul-off / velocity at die exit

At the die exit, the bubble has small diameter and large thickness. After that, it is converted into a large bubble with smaller thickness due to stretching by inside air as shown in Figure 2.10. This process plays an important role in molecular orientation of the film particularly in transverse machine direction which affects the ability of TD shrink. The nip roll speed also controls the velocity of film moving upward and directly affects MD shrink ability of the film [2, 4].
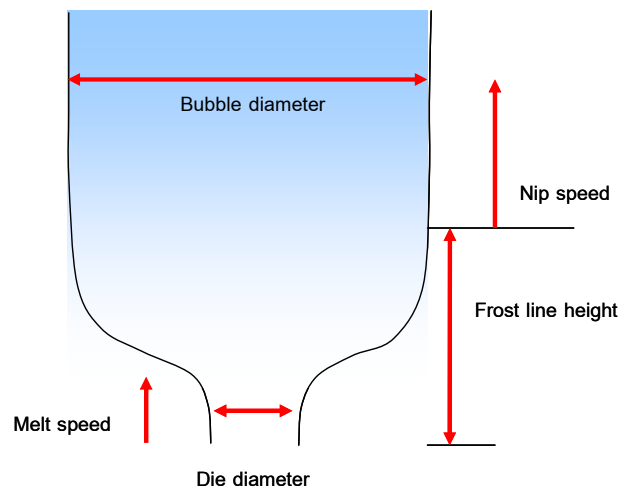
Figure 2.10 Bubble geometry

As the initial bubble diameter flows out from the die lip in the molten state, the bubble diameter is equal to the die diameter. After polymer stretching, it is cooled and becomes the solid state to form the crystallization at the same time by inside and outside air. The distance from the die exit to the regional stable bubble where the polymer begins to solidation is called the frost line height. It is also determined that the frost line height is the die exit to the lowest point of the maximum bubble diameter or no further stretching above this point. The bubble region below the frost line is normally called the stalk or neck, for example HDPE required a high-neck or long stalk extrusion because it has low melt strength when compare to LDPE.

2.2.6 Bubble cooling

In blown film process, air ring as shown in Figure 2.11 is the cooling device located circumference on the top of the die in order to cool and stabilize the outside of film bubble. This cooling system is very important to steady the operation, provide good bubble stability, good thickness uniformity, improve film properties like tear strength, tensile strength and optical property, and particularly increase the rate of outputs. Single lip air ring is normally used to process high molecular weight or high density polymer like HDPE. This material requires a high neck or long stalk extrusion due to their weak melt strength. The long stalk expands the efficiency to stretch in transverse direction and allows higher drawdown ratios to optimize the film properties but relatively slows the rate of melt extension and low output. Figure 2.12 shows dual lip air ring designed as a primary orifice near the die lip exit in order to provide a low volume of air and a second orifice located upper is designed to provide a high velocity and a large volume of air leading to enhance high output with a gauge uniformity and good bubble stability.

Figure 2.11 A blown film air ring
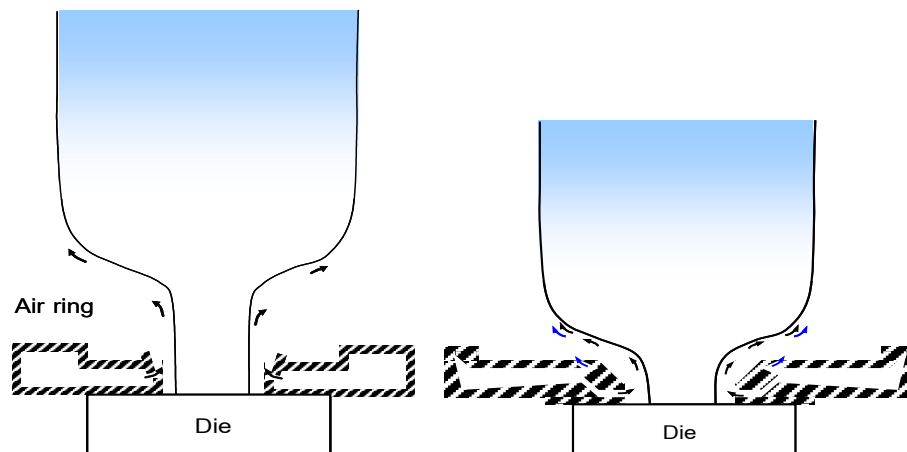
Figure 2.12 Single and dual lip air ring

PE materials tend to have the specific heat value more than other polymers. It has a specific heat in the range of 1.8-2.3 kJ/kg$^{\circ}$C while other polymers have the specific heats in the range of 0.9-1.5 kJ/kg $^{\circ}$C. Therefore, high cooling towers with high efficient cooling system are necessary for removing retain heat in the film in order to prevent the two sides from adhering together while passing through the nip rollers [10]. Today, many blown film extrusion lines employ an internal bubble cooling (IBC) system as shown in Figure 2.13 to increase cooling efficiency and production rates. It is a continuous heat exchanger, bringing cool air into the bubble while removing heated air

from inside the bubble [11]. The IBC system is very important in order to control the inlet and outlet airflows inside the bubble for cooling improvement particularly very weak melt strength materials and eliminate the bubble instability results in good thickness variation.

Figure 2.13 Internal bubble cooling (IBC)

2.2.7   Bubble stabilization

Since the movement of the bubble during blowing up results in non-uniform thickness of the film, the bubbles are usually stabilized using bubble guide and cages in order to minimize wrinkles, bagginess, tacky film and excessive friction as shown in Figure 2.14. Bubble guide and cage assembly for blown film are necessary particularly at the high output to guide and support the film above the frost line. Film scratching and bubble instability can occur when these devices do not perform properly. Generally, cage rollers are coated by teflon or nylon in order to reduce friction while a large diameter-roller can rotate easier than smaller diameter due to large surface contact. Additionally, the cage height and diameter can be adjusted to stabilize the bubble at different frost line heights and blow up ratios which suitable for different films. In the blown film process, it should be checked regularly to assure that the cage rollers can rotate freely before operating.

Figure 2.14 A bubble stabilizing cage with Teflon-coated rollers

2.2.8   Collapsing frames

A collapsing frame is provided to change moving tube of plastic material from a circular to flattened form as shown in Figure 2.15. The properly collapsing geometry can reduce the gauge non-uniformity, wrinkles and center sag of the obtained film. The height and entry angle of this device can be adjusted for in order to provide a smooth transition. The collapsing surface widely used in blown film industry is made of wooden slats and Teflon-coated rollers because of their low friction, high temperature resistant, low generation of static electricity and little maintenance requirement. High crystallinity or high stiffness polymers such as HDPE, rigid PVC, polyester, nylon and polystyrene should be preheated to increase the flexibility during collapsing and to avoid the wrinkles.

Figure 2.15 Collapsing frame

2.2.9   Haul-off

A pair of nip rollers or the haul-off device is used to pull the film up from the die and provide uniform film tension. It is located at the top of machine as shown in Figure 2.16. One of the nip roll is normally used rubber-covered and other one is fixed at a position with motor-driven to establish the line speed. This device controls film thickness, bubble diameter and frost-line height. When the haul-off speed increases, film thickness decreases. Nip rolls should be located at the top in order to ensure the complete cooling and prevent the film from blocking together. In blown film process, the film is stretched in two directions for machine and transverse directions. The drawn down rate in the axial direction can be controlled by the speed of nip roll.

Figure 2.16 A pair of nip rolls with a rubber–covered contact roll

2.2.10 Winders

From Figure 2.17, it can be seen that winders are used to collect the film by transformation from flattened into rolls which is easier to handle. The basic winding process of the film composes of the center winding and the surface winding [2]. The web tension is obtained by the spindle torque through the center of the roll for center winding process. This type can wind softer rolls and fast cycle time but it has a limitation of maximum roll diameter. For surface winding process, the winding rolls are loaded against the winding drum. This type is properly for winding very large diameter roll and minimizing waste during transfers.

Figure 2.17 A dual-station turret winder

2.3 Applications of plastic films

Plastic films are used in many applications including both food and non-food packagings such as agricultural, medical, structural, liner and industrial products. The popular thermoplastic resins widely used for film applications both in the form of monolayer and multilayer include polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), polyamide (PA), polyester (PET) and polystyrene (PS). They can be categorized based on the application requirement into three types: food packaging, non-food packaging and non-packaging films.

2.3.1 Food packaging

The primary functions of food packaging applications are related to safety in direct food contact, barrier properties to preserve food, high hot tack and good sealing through the contamination during loading some foods like sugar, coffee and oil into plastic bag. For example, fresh meats are packed in tray and often covered with stretch or shrink film that are mostly made from flexible PVC and PE shrink film. Frozen foods require high barrier shrink bags that can provide low temperature performance. These bags are based on co-extrusion of LLDPE, EVA and EVOH. Dry food applications such as cereal, cracker also require good moisture barrier and good seal performance of the sealant layer or peelable seal for easy-opening. These requirements are most often satisfied by co-extrusion of HDPE with a lower temperature sealant material such as EVA copolymers and ionomer that are the popular sealant materials. For snack food packaging such as chips, candy and cookies are dominated by oriented PP films due to their clarity, barrier, modulus, sealability, good optical property, moisture resistant and tear property. If higher barrier is needed for some snacks, metalized films or other barrier techniques are incorporated into the structure [2].

2.3.1.1 Barrier films

Barrier films are often made of multilayer films or laminated with other films for additional barrier functionality. They are designed to be impervious to gas migration and prevent penetration of liquid or water due to the small pores size of their structure. Barrier films are durable and flexible. Barrier films are used to prevent a wide variety of chemicals, moisture, oxygen and odor for protective clothing and packaging applications. In the food industry, the inner layer of packaging films is generally made of PE sealing layer. The middle barrier layer is made from metal foil, aluminum foil or film sputtered aluminum which are the most effective gas barrier materials. Moreover, nylon and EVOH are used as transparent plastic barrier layers. Some common examples of barrier film packagings are found in potato chips, meat, cheese, sausage, health care, pharmaceutical and other industrial products.

2.3.1.2 BOPP films

Oriented polypropylene (OPP) is designed for flexible packaging and labeling applications. Bopp is a bi-axially OPP film that is stretched in both machine and transverse machine directions in order to improve stiffness, tensile strength, optical property and water barrier property [12]. These films can be used in the forms of monolayer or coextruded structures, transparent or opaque, metalized or laminated with other materials. BOPP has the advantage of being non-toxic and very thin film ranging from 15 to 30 microns. It is used in food packaging applications and other products such as pressure sensitive tapes, labels, stationery, metallizing, consumer products, gift and flower wrapping, paper lamination, packaging pouches, packaging bags, electronic packaging and industrial packaging.

2.3.1.3 Breathable films

Breathable films are made of PP or PE compounded with a mineral filler. They are stretched in mono or biaxial orientations in order to create micropores during cast film or blown film processes. Breathable films have ability to allow the gases to escape but retain the larger water molecules and inhibit the dehydration process. Other important characteristics of breathable films are high strength, high resistance to puncture and excellent resistance to hydrolysis. They extend shelf life by limiting oxygen supply, reduce the live product's respiration rate and retard spoilage. They can be used for roofing applications in the construction industry and in the medical industry for bandages wound dressings, surgical drapes [12].

2.3.1.4 Laminated films

Lamination is a manufacturing method to bond the substrate material to the same or different materials like paper, fabric, aluminum or metal foil and a wide variety of plastic films in order to improve some properties such as decorative appeal, flexibility,

chemical resistance, mechanical strength, printability and barrier property. Seven methods for lamination are widely used depending on the type of raw material and application. These methods includes thermal, hot-melt, non solvent, wet, dry, extrusion coating and co-extrusion lamination [13]. For example, aluminum foil has a good barrier property but very easy to wrinkle. It can be laminated to paper on one side for increasing mechanical strength and decreasing breaks or wrinkle while it can be laminated to PE on the other side for improving heat seal property. Laminated films are commonly used for a wide variety of food packaging such as dried food such as cookies, snacks, potato chip, candies, chocolates, chewing gum and liquid food packaging such as sauce, mayonnaise, noodle soup, jams, mustard paste and oil.

2.3.2 Non-food packaging

Shrink and stretch films are used majority for non-food packaging both unitized and palletized goods. Stretch films are generally based on LLDPE produced by cast film process, while shrink film is made of LDPE produced by blown film process. Stretch films provide excellent stretch ability, clarity and puncture resistant in order to keep and protect the palletized goods during storage in warehouse and transportation. Furthermore, other non-food packaging films belong to the liner category, greenhouse film, medical packages, heavy duty sacks for packaging insulation, resin, chemicals, fertilizer, salt, pet food and plastic granule. These films require tear and impact strength, sealability, creep resistant, barrier and dart impact properties obtained from the composition of LLDPE and LDPE monolayer.

2.3.2.1 Shrink labels

Shrink label is described as an oriented plastic film sheet or tube printed on the surface to present the brand of manufacturer and improve the product decoration. These films must be superior in transparency and excellent shrink ability particularly in transverse direction in order to cover surrounding of the individual product after heating.

The most common material used for shrink labels is PVC due to its lower cost, wide range of shrink ratios and shrink temperature. Generally, film shrink labels are made in the range from 40 to 50 micron and widely used for packaging of household, cosmetics, medical and beverage products.

2.3.2.2 Heat shrink films

Heat shrink films are mostly made of LDPE, PVC and other polyolefin materials. They are shrunk to overwrap both individual and a group of product after heating. As the polymer molecules are pre-stretched and oriented during the processing, they maintain in this form even after cooling. For the application, when enough heat is applied, the polymer molecules of these films freely move and return to their tangled state for shrinkage. Shrink films give a glossy appearance, high sealing shrinkage, elasticity and memory properties. Typical applications of these films are used for the purposes of moisture and corrosion protection combined with the ease of handling and transportation. They are used for packaging of beverage, dairy, pharmaceutical, foods, cosmetic and chemical products.

2.3.2.3 Liner and bag films

Liner and bag films are widely used to form inner packaging layer for cans, bins, bags and boxes in order to contain food and non-food products such as industrial goods, household goods, trash bag, fast food, medical wastes, plastic pellets, various of powders and liquids materials which are moisture sensitive. These films and bags are usually made of LLDPE and a minor amount of LDPE and HDPE that are produced via blown film process [2]. The properties of these films require high hardness, high impact strength, high puncture strength, high tear resistant and good moisture barrier.

2.4 Literatures review

Many researchers have studied, developed and also designed many techniques to resolve a rapid increase in the amount of post-used plastic wastes, to decrease the thermal degradation occurring during reprocessing, to improve the final properties and to extend the shelf life of the recycled products [14-18]. For example, C.N. Kartalis and C.D. Papaspyrides [19] studied the recycling of post-used PE packaging film using the restabilization technique. The remelting restabilization technique was applied for the recycling of post-used, polyethylene packaging film. A multiple extrusion cycles procedure was performed at different reprocessing temperatures for monitoring the processing stability of the restabilized material. Furthermore, at different film blowing conditions mechanical properties were evaluated, to study the effect of restabilization on the mechanical performance of the recycled material. The results illustrate that the restabilization of PE film is very impressive in limiting the degradation effect, which is an essential prerequisite for the re-use in the original application, i.e. for closed-loop recycling.

A. Choudhury and M. Mukherjee [20] studied the thermal stability and degradation of post-use reclaim milk pouches during multiple extrusion cycles. In the present study, the recyclability of the post-use milk pouches (50/50 LDPE–LLDPE blend) was evaluated with or without adding stabilizer. Thoroughly washed and dried post-use milk pouch films were extruded five times at high temperature (483–513 K) in the open atmosphere. The mode of degradation during extrusion operation was studied by melt flow index (MFI), rheological properties, gel content and FT-IR analysis. The differential scanning calorimetry (DSC) analysis was carried out to evaluate the thermal stability of the stabilized and un-stabilized recycled mass from post-use milk pouch under this investigation. Mechanical properties (tensile strength,%elongation at break, tensile modulus and hardness) of the un-stabilized extruded material were significantly affected as a result of thermooxidative degradation during extrusion in presence of air. After all, stabilization with 0.4% anti-oxidant satisfactorily retains all the initial properties of the recycled material.

E.M. Abdel-Bary et al. [21] studied the recycling of polyethylene films used in greenhouses-development of multilayer plastic films. The recycling of greenhouse plastic films was carried out by coextruding two-layer plastic films. The top layer consists of a blend of virgin thermoplastic resins stabilized with different stabilizers. The bottom layer was composed mainly of PE waste in combination with virgin resins and other ingredients. The two-layer films produced were subjected to accelerated UV ageing and to outdoor weathering in two different locations for almost 1 year. The results obtained revealed that the optimized two-layer films can be successfully used as greenhouse films.

T. Dintcheva and L. Mantia [22] also studied the reprocessing and restabilization of greenhouse films. From the ecological and economical points of view, reprocessing of polyethylene greenhouse films is a promising solution to reduce discarded materials and to produce useful, or potentially useful, objects for service. Films exposed outdoors, however, show inferior mechanical properties and the melt processing worsens these properties. The addition of stabilizers and antioxidants to recycled plastic products prevents inherent thermal instabilities from occurring within the time frame of proper processing. In this study, we attempt to explore ways for improving product performance by the addition of four different additives when the recycled films undergo intensive shear processing. The process is evaluated by measuring the changes in chemical structure (carbonyl evolution) as well as rheological and mechanical characteristics (tensile properties). The effectiveness of the various additives was estimated and the one with the best antioxidant ability was identified. The analysis of processing conditions allowed us to find that the best results are emphasized by the continuous addition of the stabilizer at each step of reprocessing.

M. Di Paola and S. Papa [23] also studied the characterization of aluminized polyethylene blends via mechanical recycling. The use and consumption of polymeric resins is growing around the world because they are easily formed, and can be used in a variety of applications. The increasing consumption results in a great environmental impact because the used plastics are discarded in nature in a nonrational form. Facing

all these problems, recycling becomes a powerful strategy regarding the reduction of the environmental impact caused by plastic waste. In this work polymeric blends were prepared by mechanical recycling and characterized. LDPE/Al residues from cartooned packaging were blended with recycled HDPE/LDPE and virgin PE resins. It was observed that processability, mechanical properties, chemical resistance and water absorption are dependent on the blend compositions. Also, an aluminum film was found to remain as isolated particles in the polymeric matrix and the mechanical behavior of the blend depends on the aluminum dispersion. Either, the blend water absorption depends on recycled material contamination, mainly polyamides. Finally, the amount of recycled material added to the blends determines both chemical stability and thermal characteristics.

M. Run et al. [24] studied the nonisothermal crystallization and melting behavior of mPE/LLDPE/LDPE ternary blends. Nonisothermal crystallization kinetics of ternary blends of the metallocence polyethylene (mPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) were studied using DSC at various scanning rates. The Ozawa theory and a method developed by Mo were employed to describe the nonisothermal crystallization process of the two selected ternary blends. The results speak that Mo method is successful in describing the nonisothermal crystallization process of mPE/LLDPE/LDPE ternary blends, while Ozawa theory is not accurate to interpret the whole process of nonisothermal crystallization. Each ternary blend in this study shows different crystallization and melting behavior due to its different mPE content. The crystallinity of the ternary blends rises with increasing mPE content, and mPE improve the crystallization of the blends at low temperature. The crystallization activation energy of the five ternary blends that had been calculated from Vyazovkin method was increased with mPE content, indicating that the more mPE in the blends, the easier the nucleus or microcrystallites form at the primary stage of nonisothermal crystallization. LLDPE and mPE may form mixed crystals due to none separated-peaks were observed around the main melting or crystallization peak when the ternary blends were heating or cooling. The fixed small content of LDPE made little influence on the

main crystallization behavior of the ternary blends and the crystallization behavior was mainly determined by the content of mPE and LLDPE.

R. W. Halle et al. [25] studied downgauge paper overwrap films using mLLDPE blends. Downgauging is a continuing trend in the evolution of the films used to package paper products, such as toilet paper, napkins, and paper towels. As is usual in almost all downgauging efforts, a basic goal of the film redesign process is that any decrease in film thickness be accomplished with little or no loss in film properties, such as stiffness, clarity, and puncture resistance. A study of blends of mLLDPE with a medium molecular weight HDPE has shown that downgauged films can be designed with properties comparable to today's overwrap films. These mLLDPE-HDPE blends open new avenues to film formulation where film toughness and stiffness must be maintained while film thickness is reduced.

In these recent years, the addition of a filler into polymer matrix is the commonly used method for improving the mechanical properties of a polymer. Furthermore, adding some types of the fillers is for the purpose of reducing the consumption of virgin polymer used. Many types of fillers have been used including carbon black, calcium carbonate, glass fiber, wood fiber, silica and clays. The most important commodity filler widely used in various polymers is calcium carbonate due to its availablity at low cost in a variety of particle shapes and sizes [26-28]. However, there are many significant factors which influence the final properties of filler-added polymer such as the mineral factors (morphology, size distribution, surface chemistry, and chemical purity), polymer factors (molecular weight, molecular weight distribution, branching type and distribution, degree of crystallinity, polymer chemistry and polarity) and the performance of mixing process which can result in a good dispersion of a filler into the polymer matrix [29-30]. Some studies also demonstrated that the surface treated filler has a potential improvement of processability and filler distribution in the polymer mixing. However, several studies have successful demonstrated an increase in mechanical property by adding the fillers in the common polymers such as PP and PE. For example, C.M. Chan et al. [31] studied polypropylene/calcium carbonate nanocomposites.

Polypropylene (PP) and calcium carbonate nanocomposites were prepared by melt mixing in a Haake mixer. The average primary particle size of the $CaCO_3$ nanoparticles was measured to be about 44 nm. The dispersion of the $CaCO_3$ nanoparticles in PP was good for filler content below 9.2 vol%. Differential scanning calorimetry (DSC) results indicated that the $CaCO_3$ nanoparticles are a very effective nucleating agent for PP. Tensile tests showed that the modulus of the nanocomposites increased by approximately 85%, while the ultimate stress and strain, as well as yield stress and strain were not much affected by the presence of $CaCO_3$ nanoparticles. The results of the tensile test can be explained by the presence of the two-counter balancing forces-the reinforcing effect of the $CaCO_3$ nanoparticles and the decrease in spherulite size of the PP. Izod impact tests suggested that the incorporation of $CaCO_3$ nanoparticles in PP has significantly increased its impact strength by approximately 300%. *J*-integral tests showed a dramatic 500% increase in the notched fracture toughness. Micrographs of scanning electron microscopy revealed the absence of spherulitic structure for the PP matrix. In addition, DSC results indicated the presence of a small amount of β phase PP after the addition of the calcium carbonate nanoparticles. We believe that the large number of $CaCO_3$ nanoparticles can act as stress concentration sites, which can promote cavitation at the particle–polymer boundaries during loading. The cavitation can release the plastic constraints and trigger mass plastic deformation of the matrix, leading to much improved fracture toughness.

G. Levita et al. [32] studied marchetti fracture of ultrafine calcium carbonate/polypropylene composites. The strength and fracture properties of a polypropylene filled with ultrafine calcium carbonate (0.07 m) have been studied in the composition range of 0 to 40 percent by volume. Untreated and surface treated (with stearic acid and a titanate coupling agent) grades have been considered. The untreated filler caused a decrease of toughness whereas a maximum, at 10 percent, was observed for the treated filler. The fracture energy was analyzed in terms of the crack pinning model. Due to the very small size of particles the pinning contribution proved to be negligible.

P. Mereri et al. [33] studied the mechanical behavior of polypropylene composites containing fine mineral filler. The inclusion of mineral fillers in thermoplastics improves some mechanical properties but reduces others, such as impact strength. However, the use of ultrafine fillers limits this degradation. The influence of two surface treatments on the mechanical properties of polypropylene/ultrafine-kaolin composites was studied. In the first treatment, stearic acid was used on dry powder, and the second was a cationic treatment with quaternary ammonium in suspension. An improvement in the impact strength was found when the second agent was used. This can be explained from both macroscopic and microscopic points of view. We observe a better particle dispersion in the matrix and thermal analysis indicates that the crystalline structure of these materials is finer. In addition, tensile tests carried out on matrix/agent blends show that a soft interface around each particle could act as a shock absorber during an impact test

J.F. Chen et al. [26] studied toughening of polypropylene-ethylene copolymer with nanosized $CaCO_3$ and styrene-butadiene-styrene. Nanocomposites of nanosized $CaCO_3$/ polypropylene-ethylene copolymer (PPE) and nanosized $CaCO_3$/PPE/styrene-butadiene-styrene (SBS) were prepared by using a two-roll mill and a single-screw extruder. By adding $CaCO_3$ nanoparticles into the PPE matrix, the toughness of the matrix substantially improved. At a nanosized $CaCO_3$ content of 12 phr (parts per hundred PPE resin by weight), the impact strength of $CaCO_3$/PPE at room temperature reached 61.6 kJ/m^2, which is 3.02 times that of unfilled PPE matrix. In the nanosized $CaCO_3$/PPE/SBS system, the rubbery phase and filler phase are independently dispersed in the PPE matrix. As a result of the addition of nanosized $CaCO_3$, the viscosity of PPE matrix significantly increased. The increased shear force during compounding continuously breaks down SBS particles, resulting in the reduction of the SBS particle size and improving the dispersion of SBS in the polymer matrix. Thus the toughening effect of SBS on matrix was improved. Simultaneously, the existence of SBS provides the matrix with a good intrinsic toughness, satisfying the condition that nanosized inorganic particles of $CaCO_3$ efficiently toughen the polymer matrix. The synergistic toughening function of nanosized $CaCO_3$ and SBS on PPE matrix was exhibited.

Y. Kun et al. [34] studied morphology and mechanical properties of polypropylene/calcium carbonate nanocomposites. Three polypropylene (PP) matrices with different intrinsic toughness were used to study the morphology and mechanical properties of polypropylene filled with nano-sized calcium carbonate particles. PP1 was a homopolymer, PP2 was a propylene-ethylene copolymer, and PP3 was a mixture of PP1 and PP2 (PP1:PP2 = 1:1, weight ratio). The precipitated calcium carbonate (CC0.07) with an average particle size of 0.07 um was used. Only the yield strength of PP1 nanocomposites filled with low CC0.07 contents (from 2 to 10 wt.%) could increase. When the CC0.07 content was appropriate, the impact strength of all three PP nanocomposites could improve. It was interesting that the intrinsic toughness of PP matrix would influence the toughening effect of the nanoparticles. Only in the case of the moderate matrix toughness (PP3 matrix), the nanocomposites could receive the highest extent of toughness increase (4.3 times that of matrix).

A.O. Maged et al. [35] studied the Influence of excessive filler coating on the tensile properties of LDPE–calcium carbonate composites. Calcium carbonate filler is usually coated with stearic acid to reduce their surface energy and improve their dispersion in polymers. Commercial product is often over-coated and contain an excess of surfactant. It was found that stearic acid linearly increases the modulus and yield stress of LDPE but reduces its tensile strength, yield strain, and ultimate elongation. The influence of surfactant excess on the tensile properties of low-density polyethylene (LDPE)-$CaCO_3$ composites was investigated. Compounds of LDPE and optimally coated filler or with excess surfactant were prepared and their properties compared. $CaCO_3$ increased the stiffness and yield stress of the polymer but reduced all its other tensile properties. Over-coating the filler did not lead to linear accumulation of the effects of filler and stearic acid on the polymer matrix. In fact, surfactant excess amplifies the reinforcing effect on the stiffness but reduces all other mechanical properties of the composite. Calcium stearate, which is sometimes used as acid scavenger, lubricant or processing aid, has the same effect on the polymer properties as stearic acid, but to a smaller extent. It is concluded that it is most advantageous to coat the filler with the

optimal amount of surfactant necessary to cover its surface with an organic monolayer unless the influence of excessive coating is required for a certain application. Care must also be taken in interpreting some of the published results, where the quality of the filler coating was not investigated.

Z. Bartczak et al. [27] studied high-density polyethylene toughened with calcium carbonate filler particles. Here we extend the investigation described in the preceding companion communication. To rectify its notch brittleness, high-density polyethylene (HDPE) was modified by rigid particulate fillers consisting of three different sizes of $CaCO_3$ particles of 3.50, 0.70 and 0.44 μm weight average diameter in various volume fractions. Mechanical properties including notched Izod impact energy of the extrusion-blended/injection-moulded samples were examined as a function of filler particle size and filler volume fraction. In exactly the same manner as exhibited by the rubber particle-modified compositions described in the previous communication, the toughness of the $CaCO_3$-filled materials increased dramatically when the mean interparticle ligament thickness of the matrix polyethylene dropped to values below 0.6 μm. The stiff fillers used in this study provided the unusual additional benefit of substantially increasing the Young's modulus of the compounds while also dramatically improving their impact energy.

K. Sangmin et al. [36] studied tensile property and interfacial dewetting in the calcite filled HDPE, LDPE, and LLDPE composites. Mechanical properties and complex melt viscosity of unfilled and the calcite (calcium carbonate: $CaCO_3$) filled high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE) composites using dumbbell bar and film specimens are studied. In addition, the formation of air holes between calcium carbonate and the resin matrix was investigated from the phase morphology and interfacial behavior between the above constituents upon stretching using scanning electron microscopy. The tensile stress and the complex melt viscosity of the calcite filled (50%) polyethylene composites were higher than that of unfilled ones, implying that the reinforcing effect of calcium carbonate. The crack was initiated up to first 50% elongation along the transverse direction and the formation of air holes was originated by dewetting occurring through machine direction in the interface between calcium carbonate surface and HDPE. The

propagation mechanism of the air hole formation was proposed to firstly originate by dewetting up to 300% elongation, and enlarged not only by breaking of a superimposed fibril structure, but also by merging effect air holes between fibrous resin matrix. However, the crack propagation was not observed at the very beginning elongation for the calcite filled LDPE and LLDPE systems. Less fibril structure was observed in LLDPE, then LDPE composites. The observed shape and the average size of the air holes were different from system to system. This sort of different interfacial behavior and mechanical properties may arise from different configuration of polyethylene.

L. Alicia et al. [37] studied the optical properties of $CaCO_3$-filled poly(ethylene-co-vinyl acetate)films. Optical properties, such as transmittance and diffuse reflectance in the range of 200-800 nm, of hot-pressed films of poly(ethylene-co-vinyl acetate) filled with up to 10 wt% of calcium carbonate were analyzed. A linear relationship between optical properties and film thickness was found for these composites. In the range of compositions analyzed, transmittance of films decreases with an increasing in the filler content following an exponential law. The amount of decreasing can also be related to the average statistics particle diameter for a constant weight fraction of added filler by a square root law. Diffuse reflectance of the films was very low in the visible zone and increases considerably in the UV zone.

CHAPTER III

EXPERIMENT

3.1 Materials

Types, origins and specifications of the materials used in this research are summarized in Table 3.1. All materials were used as received.

Table 3.1 Types, origins and specifications of the materials

Types	Grade	Company	Density (g/cm^3)	MFI (g/10min)	Tensile strength (ASTM D882) (MPa)		Elongation (ASTM D882) (%)	
					MD	TD	MD	TD
LDPE	D2022	TPIPL	0.920	0.23	31.8	28.9	470	660
MDPE	FB2310	Borouge	0.931	0.20	50	40	550	800
LLDPE	2009FA	SCG	0.920	1.00	37.28	34.34	1000	1200
re-LDPE	-	Sunsea P.S.	-	0.31	-		-	
CaCO$_3$	CAE06	PolyMerit Asia	1.5	-	-		-	

3.2 Blown film co-extrusion

Three layered films were prepared by Reifenhauser blown film co-extrusion machine as shown in Figure 3.1 using the blow up ratio (BUR) and the output rate of 2.73 and 280 kg/hr, respectively. The processing temperatures were controlled at 185 to 195 $^\circ$C for every zone of each screw. Die diameter, die gap and film width were set at 350 mm, 2.59 mm and 1500 mm, respectively. The thickness of the middle layer was 75 micron while the thickness of each outer layer was 37.5 micron. Therefore, overall film thickness was 150 micron.

Figure 3.1 Reifenhauser blown film co-extrusion machine

3.2.1 Procedure

Polymer resins and/or filler were automatically loaded into gravimetric dosing hoppers as shown in Figure 3.2 and automatically weighed before transferring into the barrels containing single screws.

Figure 3.2 Gravimetric dosing hoppers

After weighing, polymer resins were moved forward into the barrels by motor driving as shown in Figure 3.3. The high processing temperature and high shear stress between the screw and the barrel caused the polymer resins to melt. All of homogeneous polymer melts from each extruder were then fed into the vertically single stack die. Within the die, the various flow streams of the individual layer were combined to form a single-ply film. They did not mix but retained their compositions within the combined flow stream because of their high viscosity.

Figure 3.3 Three barrels of co-extrusion machine

A single-ply of molten polymer flowed out from the vertical die lip in the form of a freely bubble going up through the height cooling tower. The bubble tube was simultaneously cooled by the air from external air ring and internal bubble cooling (IBC) unit as shown in Figure 3.4. The molten tube gradually deformed into a stable solid cylindrical bubble beyond the frost line height and generated crystallization. Then, it was gradually flattened in the collapsing device consisting of a pair of the rollers.

Figure 3.4 External air ring and internal bubble cooling (IBC)

The flattened film was pulled up by the nip rolls, which brought the flattened film through the pair of chill rollers and the secondary nip rolls. A combination of high internal air pressure led to the stretching of the film bubble in cross orientation or transverse machine direction (TD). In other words, the nip roller winding controlled the film orientation in machine direction (MD). Suitable blow up ratio and take-off speed setting could result in a balanced molecular structure orientation and a good property of final film products. Finally, the film tube was separated to a film sheet by edge trimming process before winding as shown in Figure 3.5.

Figure 3.5 Edge trimming before winding

3.2.2 Film formulations

In this research, the studies of three layered shrink film preparation were separated into three parts. The first part emphasized on the preparation of the films by blending virgin LDPE with re-LDPE resin in the middle layer in order to study the possibility of using re-LDPE instead of LDPE. The compositions were varied as given in **Table 3.2**.

Table 3.2 Three layered film formulations based on LDPE and re-LDPE blends.

No	Composition of each layer (wt%)		
	Outer	Middle	Outer
1	LDPE (100)	LDPE (100)	LDPE (100)
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)
6	LDPE (100)	re-LDPE (100)	LDPE (100)

The aim of second part was to improve the mechanical properties of the films based on re-LDPE by blending re-LDPE with MDPE in the middle layer. The compositions were varied as given in **Table 3.3.**

Table 3.3 Three layered film formulations based on re-LDPE and MDPE blends.

No	Composition of each layer (wt%)		
	Outer	Middle	Outer
1	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)
2	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)
3	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)
4	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)

In addition, the improvement of the mechanical properties especially seal strength by blending LDPE with LLDPE in the outer layer was also investigated. The compositions were varied as given in **Table 3.4.**

Table 3.4 Three layered film formulations based on LDPE and LLDPE blends.

No	Composition of each layer (wt%)		
	Outer	Middle	Outer
1	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)
2	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)
3	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)
4	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)

The final part was to study the effects of calcium carbonate addition on optical, mechanical and thermal properties of three layered films. The compositions were varied as given in **Table 3.5.**

Table 3.5 Three layered film formulations based on $CaCO_3$ filled re-LDPE

No	Composition of each layer (wt%)		
	Outer	Middle	Outer
1	LDPE (100)	re-LDPE : $CaCO_3$ (95:5)	LDPE (100)
2	LDPE (100)	re-LDPE : $CaCO_3$ (92.5:7.5)	LDPE (100)
3	LDPE (100)	re-LDPE : $CaCO_3$ (90:10)	LDPE (100)
4	LDPE (100)	re-LDPE : $CaCO_3$ (85:15)	LDPE (100)

3.3 Morphology analysis

JEOL JSM-6300F Scanning electron microscope (SEM) shown in Figure 3.6 was used to investigate the morphology of three layered films and calcium carbonate distribution in re-LDPE matrix. Three layered films were cut with a glass knife by using a technique of cryogenic ultramicrotome at the isothermal temperature of $-95^{\circ}C$ under the slow flow liquid nitrogen condition in order to prevent the structure deformation. The specimens were sputter-coated with gold under vacuum system before analyzing by SEM.

Figure 3.6 Scanning electron microscope (SEM)

3.4 Characterization of thermal behaviors

Perkin Elmer Diamond Differential scanning calorimeter (DSC) shown in Figure 3.7 was used to characterize thermal behaviors and determine the degree of crystallinity. The amount of each three layered film used was 3-5 mg. The operation was carried out under nitrogen atmosphere at the flow rate of 50 ml/min.The heating rate was set at 10°C/min starting from 50 to 200 $^{\circ}$C and cooled down to room temperature before second heating immediately at same condition. The first heating was employed in order to eliminate previous thermal history. The melting temperature (T_m) and enthalpy (ΔH) were determined and recorded.

Figure 3.7 Differential scanning calorimeter (DSC)

3.5 Determination of mechanical properties

3.5.1 Tensile properties

Tensile test in both MD and TD was carried out by a LLOYD universal testing machine according to ASTM D882. Each film was cut into 5 specimens having the size of 1.5 mm in width and 15 mm in length as shown in Figure 3.8. The tensile test was performed using a load cell of 500 N and each specimen was stretched at a drawing rate of 500 mm/min.
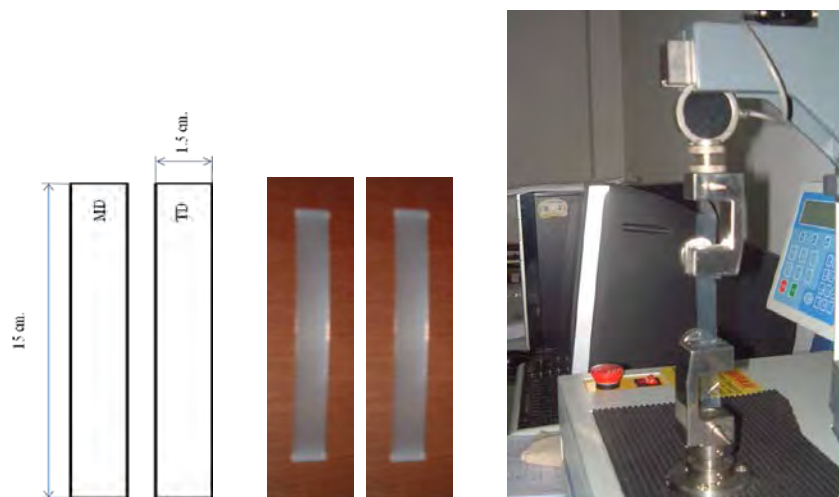
Figure 3.8 Tensile test

3.5.2 Heat seal strength

Heat seal strength in both MD and TD was determined by a LLOYD universal testing machine according to ASTM F88. All film samples were sealed under heat seal temperature of 150 $^{\circ}$C, welding time for 1 second and seal force was set at 20 psi using seal machine as shown in Figure 3.9. These films were cut into a width of 25 mm. The test was done using the extension rate of 500 mm/min, and load cell 500 N using grip separation distance at 50 mm as shown in Figure 3.10.

Figure 3.9 Seal machine

Figure 3.10 Seal strength measurement

3.6 Determination of heat shrink property

Heat shrink ability of a plastic film can be explained in the term of shrink ratio. The shrinkage measurement of three layered films was investigated according to ASTM D2732 method. The plastic films were prepared in the size of 10 cm x 10 cm as shown in Figure 3.11 and were immerged in hot oil bath at 130 $^{\circ}$C for 10 seconds as shown in Figure 3.12. After that, 5 specimens of each shrunk film were measured for the change in its dimension and the shrink ratios in both MD and TD were calculated.

10 cm.

10 cm.
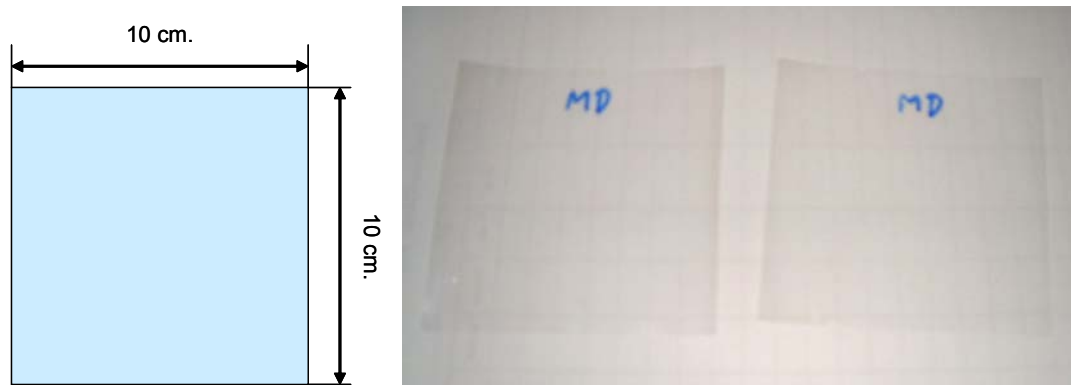
Figure 3.11 Film specimens for heat shrink measurement
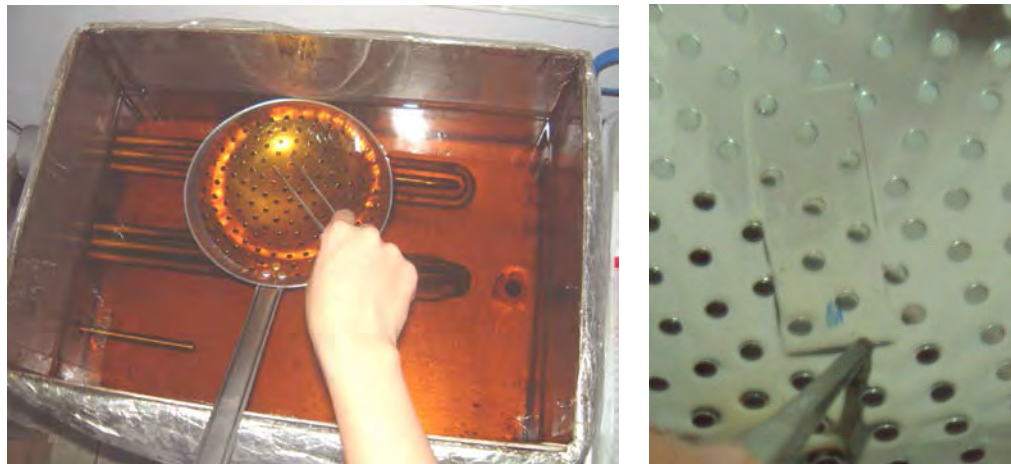
Figure 3.12 Heat shrink measurement

3.7 Determination of optical property

The effect of $CaCO_3$ on optical property of three layered films was evaluated in the terms of haze and gloss based on ASTM D1003 and D2457 using BYK Haze-Gard Plus (E0606) and BYK Gardner (D82538 geretsried), respectively as shown in Figures 3.13-3.14. 5 specimens of each film were subjected for evaluation.

Figure 3.13 Haze measurement
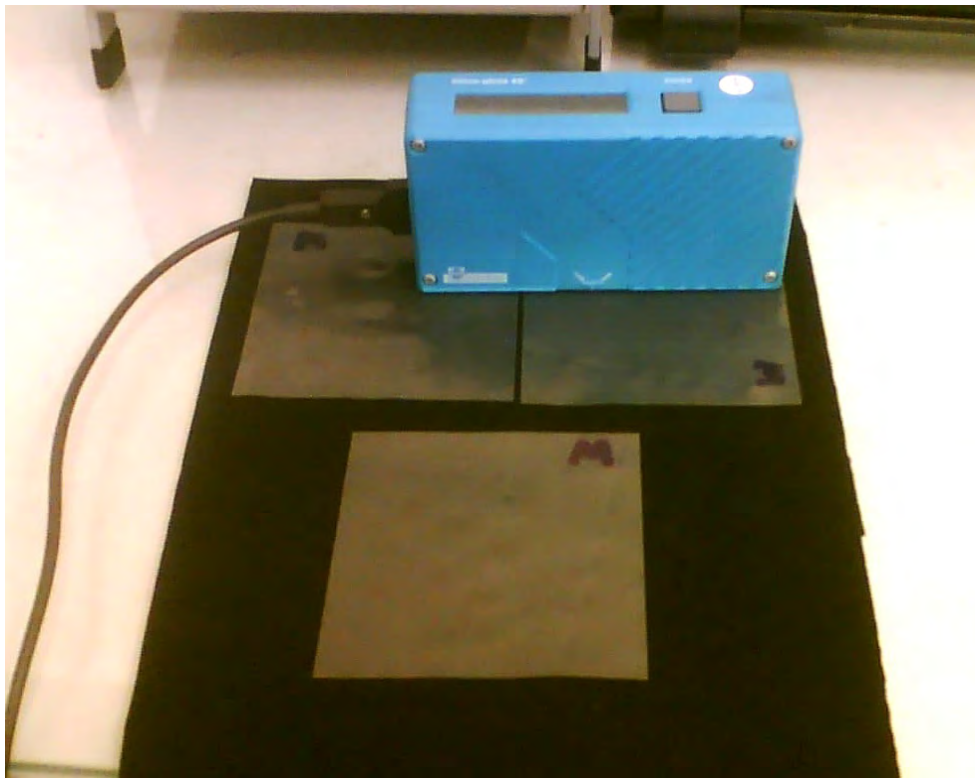
Figure 3.14 Gloss measurement

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Appearance of LDPE resins

Figure 4.1 shows the appearance of recycled LDPE resin compared to that of virgin LDPE resin. Its color is yellow due to thermal degradation which may occur during re-melting and pelletization.
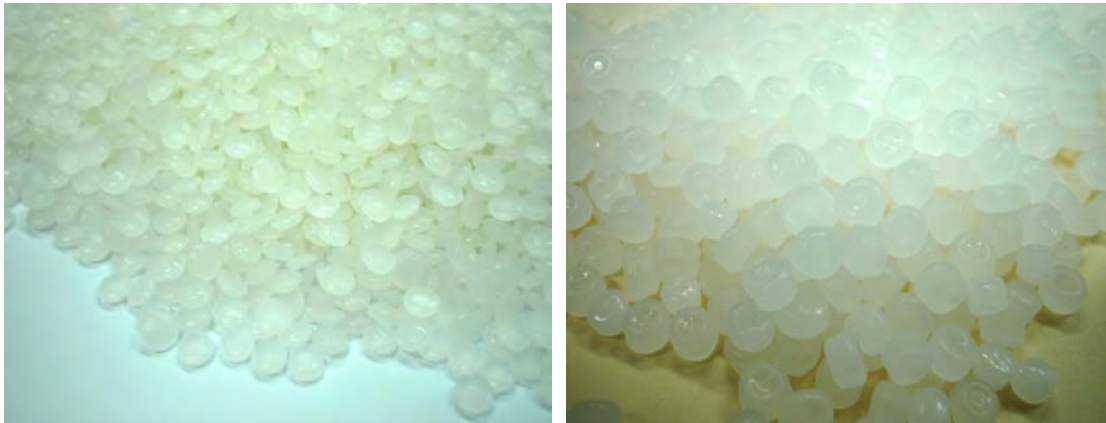
Figure 4.1 Recycled (left) and virgin LDPE (right) resins

4.2 Characteristics and properties of LDPE/LDPE-re-LDPE/LDPE films

4.2.1 Film appearance

Figure 4.2 shows the appearance of three layered shrink film specimens having LDPE and re-LDPE blend in the middle layer while the outer layers compose only of virgin LDPE. These films are transparent and have the consistencies in film width and thickness without gels, scratches or melt fractures. An increase in re-LDPE content did not significantly affect haze and gloss of the films as shown in Figure 4.3. The values of haze and gloss are reported in appendix A (Table 41, 45).
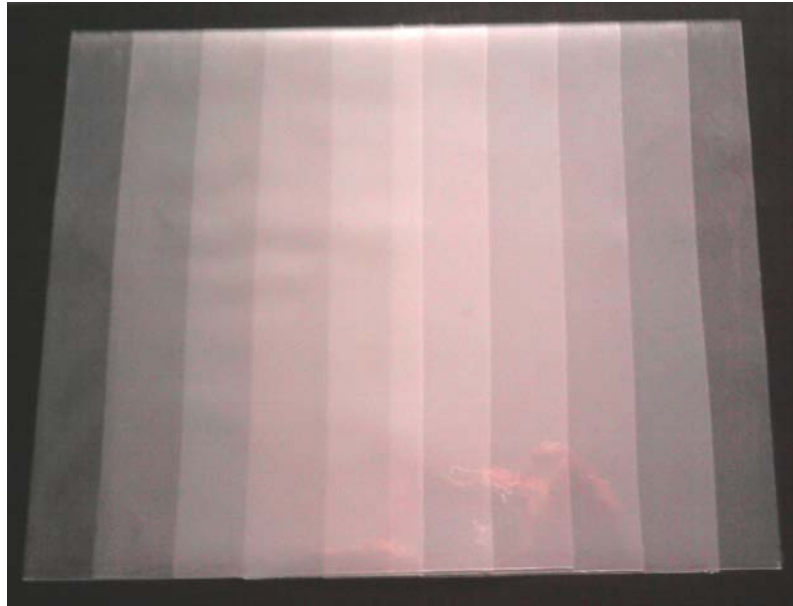
Figure 4.2 The appearance of LDPE/LDPE-re-LDPE/LDPE films
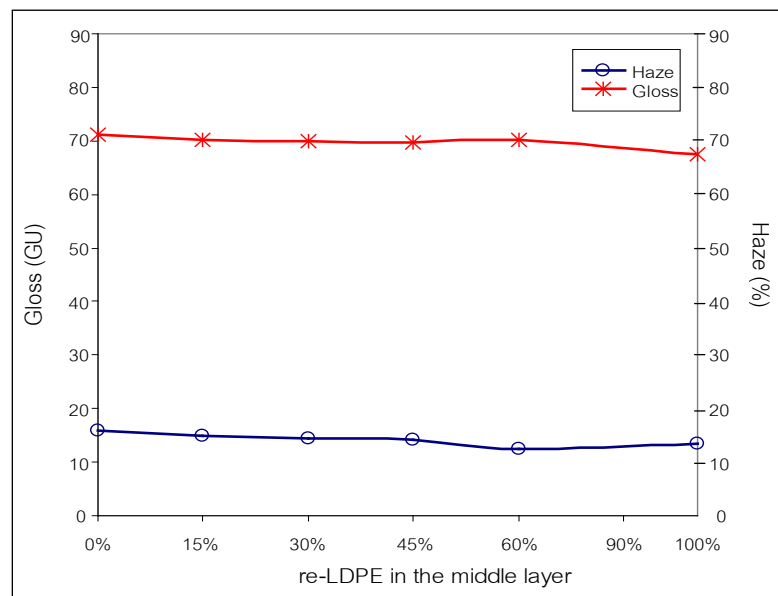
Figure 4.3 Haze and gloss of LDPE/LDPE-re-LDPE/LDPE films

4.2.2 Thermal behaviors

Thermal behaviors of three layered films can be determined by differential scanning calorimetry. This technique is used to quantify the heat flow into or flow out of a material as a function of time or temperature. The heat is reported as the percentage of crystallinity derived from the proportion against the heat of fusion for a sample material compare to a 100% crystalline of the same material. PE is a semi-crystalline polymer containing two primary components of a crystalline and an amorphous phase. The degree of crystallinity of a semi-crystalline polymer depends on several factors including average molecular weight (MW), MW distribution, degree of branching, the presence of a copolymer and the thermal history of a polymer. Consequently, the characteristics of a product made from a semi-crystalline polymer depend upon the degree of crystallinity which can be determined from $\Delta H_f / \Delta H_f^o$, where ΔH_f is defined as the melting enthalpy of a sample investigated. In this research, ΔH_f^o was defined as the melting enthalpy of 100% crystallization PE, where ΔH_f^o was 293 J/g. The enthalpy value can be obtained from the integral area of DSC heating curve [33]. DSC thermograms of LDPE, re-LDPE, MDPE and LLDPE resins in Figure 4.4 show single melting peaks. The results in Table 4.1 show that MDPE has highest melting point and %crystallinity due to its highest linearity of the molecule and highest density when compared to the others. Higher consistency in molecular structure with a large amount of short side branches of LLDPE result in higher melting point and lower %crystallinity than LDPE resin.
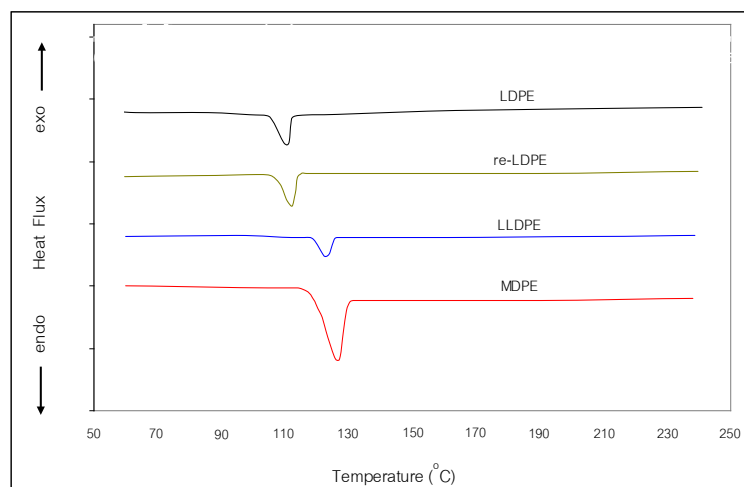
Figure 4.4 DSC thermograms of LDPE, re-LDPE, MDPE and LLDPE resins

Table 4.1 Melting temperatures and % crystallinity of LDPE, re-LDPE, MDPE, LLDPE resins

Resins	Melting Temperature T_1 (^{o}C)	Enthalpy ΔH_1 (J/g)	Crystallinity (%)
LDPE	112	66	23
re-LDPE	110	72	24
MDPE	131	92	31
LLDPE	122	63	22

DSC thermograms of all films are shown in Figure 4.5. The results demonstrate that DSC thermograms show only a single sharp peak. This evidence suggests that all blended compositions of LDPE and re-LDPE were miscible. This may be due to a good blending system and the effect of similar branching content between LDPE and re-LDPE which can improve the polymer dispersion and co-crystallization [34-35]. The melting temperatures and %crystallinity of LDPE/LDPE-re-LDPE/LDPE films are shown in **Table 4.2**. It can be seen that %crystallinity increases from 15% to 18% when re-LDPE content in the middle layer increases from 0 to 100 wt%. This may due to thermal degradation of re-LDPE which occurred during reprocessing and this resulted in a decrease in the molecular weights of the polymer backbone and its branches. Consequently, the molten polymer can flow easier which was confirmed by an increase

in MFI from 0.23 g/10min to 0.31 g/10min after reprocessing of re-LDPE. The reduction of molecular weight and molecular chain branches tends to reduce the entanglement between polymer molecules and contribute to an increase in the degree of crystallinity.
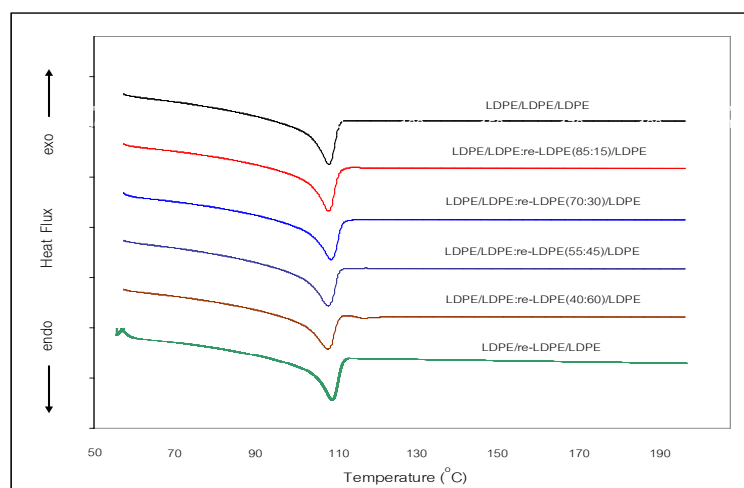
Figure 4.5 DSC thermograms of LDPE/LDPE-re-LDPE/LDPE films

Table 4.2 Melting temperatures and % crystallinity of LDPE/LDPE-re-LDPE/LDPE films

LDPE:re-LDPE (wt%)	Melting Temperature T_1 (^{o}C)	Enthalpy ΔH_1 (J/g)	Crystallinity (%)
100:0	109	45	15
85:15	109	48	16
70:30	110	48	16
55:45	109	49	17
40:60	109	51	17
0:100	110	54	18

4.2.3 Tensile properties

Figure 4.6 shows tensile strength of LDPE/LDPE-re-LDPE/LDPE films and all values are given in Appendix A (Table A1-2). It was found that an increase in re-LDPE content from 0 to 100 wt% enhances the tensile strength of the films from 13.03 to 14.79 MPa in MD and 11.23 to 14.35 MPa in TD. Normally, LDPE structure contains high MW and long chain branches. However, as a result of reprocessing, MW of re-LDPE was decreased inducing an increase in %crystallinity of the films as previously shown in **Table 4.2**. This can increase tensile strength of the films. However, Figure 4.7 shows that %elongation at break in MD is lowest when 100 wt% of re-LDPE. This may be because of a reduction of average MW in backbone chain and highest %crystallinity made the polymer molecules difficult to extend and deform. On the other hand, this can improve the rearrangement of polymer backbone chains in TD according to the ratio of stretching of the films which can increase %elongation at break in TD. All values of %elongation at break are reported in Appendix A (Table A 25-26).
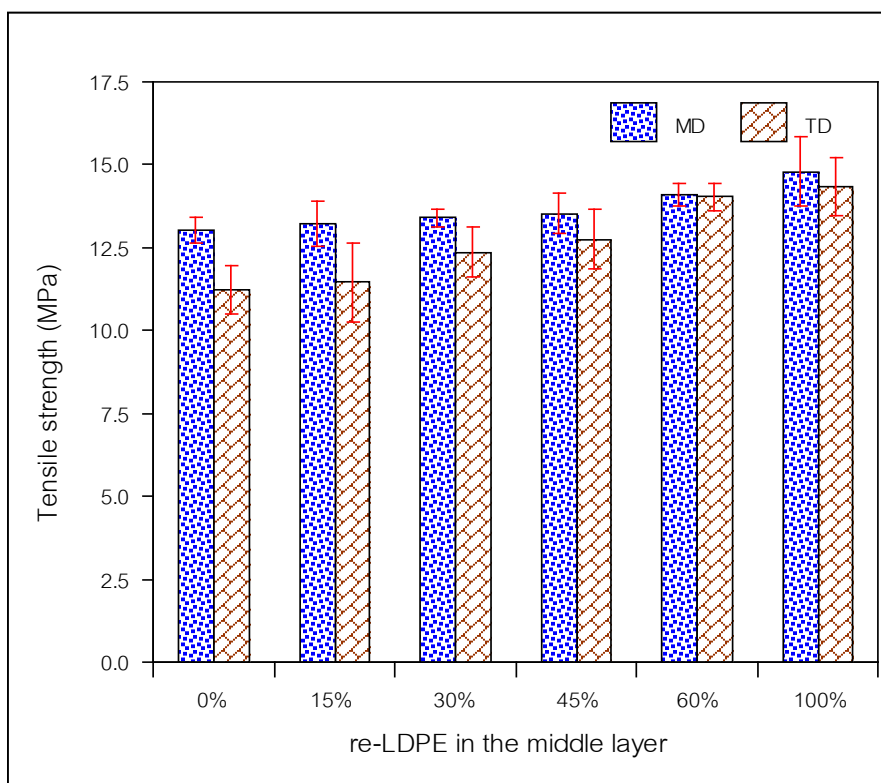
Figure 4.6 Tensile strength of LDPE/LDPE-re-LDPE/LDPE films
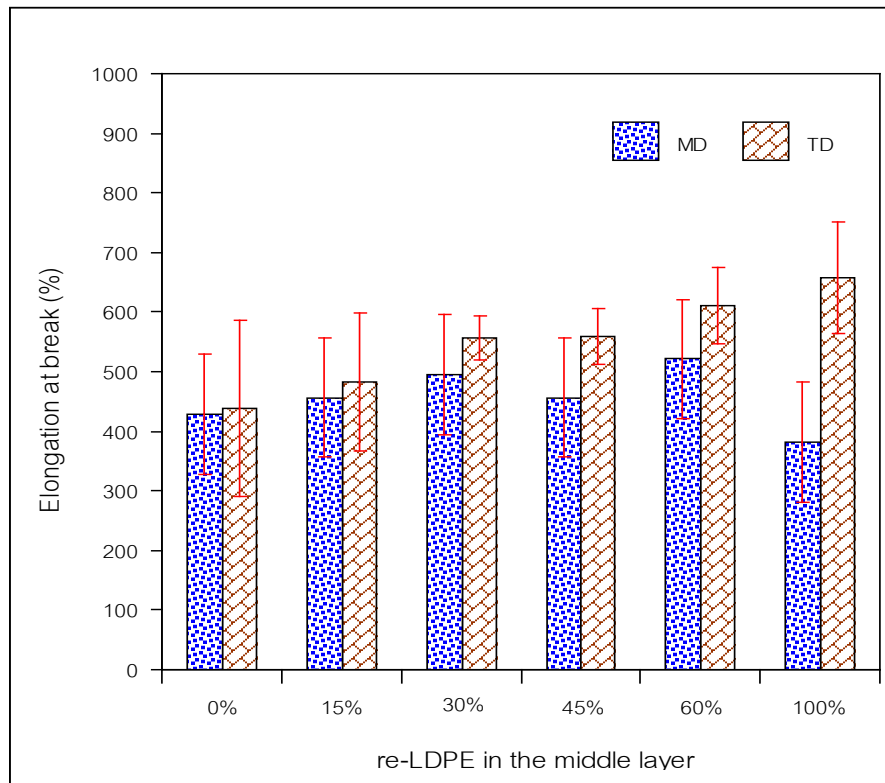
Figure 4.7 Elongation at break of LDPE/LDPE-re-LDPE/LDPE films
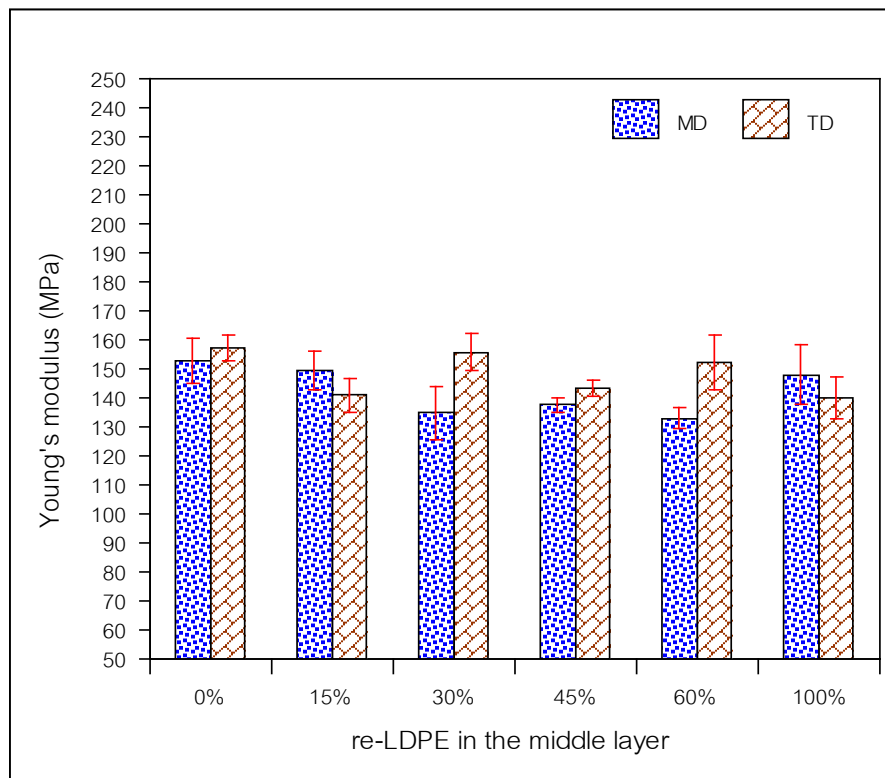
Figure 4.8 Young's modulus of LDPE/LDPE-re-LDPE/LDPE films.

Figure 4.8 shows Young's modulus of LDPE/LDPE-re-LDPE/LDPE films. It was found that at 100 %wt of LDPE, highest Young's modulus was obtained due to entanglements of long-chain branches of LDPE causing the difficulty in the movement of the polymer chains. It was expected that as re-LDPE content increased, Young's modulus should decrease because of the reduction of its MW and the length of its chains. However, this is overcome by an increase in %crystallinity. Therefore, at 100 wt% of re-LDPE, Young's modulus of the film is slightly lower than that of the film containing only LDPE. All values of Young's modulus are given in Appendix A (Table A33-34).

4.2.4 Seal strength

One of the most important properties for shrink film is heat seal ability. Heat seal can be used to extend the shelf-life of products both individual and multi-packed. Good heat seal adhesion can protect and reduce damage during storage, transportation, improve barrier property for food packaging and also reduce costs caused by packaging problems. Heat sealing is made by fusing two polymer surfaces using heat and pressure. The adhesion is promoted by applying the heat from outside. As the sealant layer begins to melt, more intimate contact or wetting of the sealing surfaces occurs. This requires the sufficient time for the polymer molecules in the crystalline regions to melt [38]. In order for heat sealing to be effective, molecular segments must diffuse across the interface to form the entanglements among two sealant layers as shown in Figure 4.9. For semicrystalline polymers, the rearrangements occur at the interface and generate re-crystallization after cooling which results in a good seal strength property [39]. Figure 4.10 shows three layered film of LDPE/LDPE-re-LDPE/LDPE specimen obtained from seal strength measurement having breaking point closed to heat seal region. It is difficult for polymer molecules having higher MW to melt and diffuse between two interfaces of sealant layers. As a result, lower seal strength is observed [40]. Since re-LDPE has lower MW than virgin LDPE; therefore, it is easier for its molecules to melt and diffuse between sealing interfaces. Consequently,

the films containing higher re-LDPE content exhibit higher seal strength both in MD and TD as shown in Figure 4.11. All values of seal strength are given in Appendix A (Table A9-10).
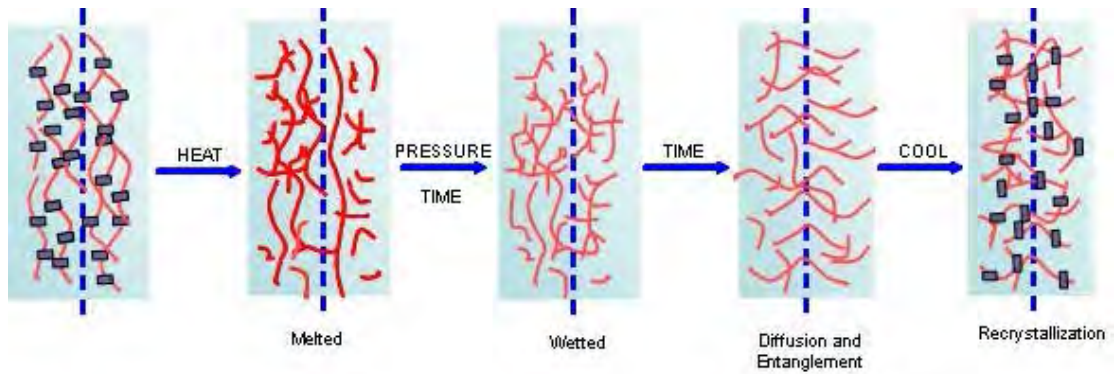
Figure 4.9 Seal mechanism

Figure 4.10 Specimen of LDPE/LDPE-re-LDPE/LDPE film after seal strength measurement
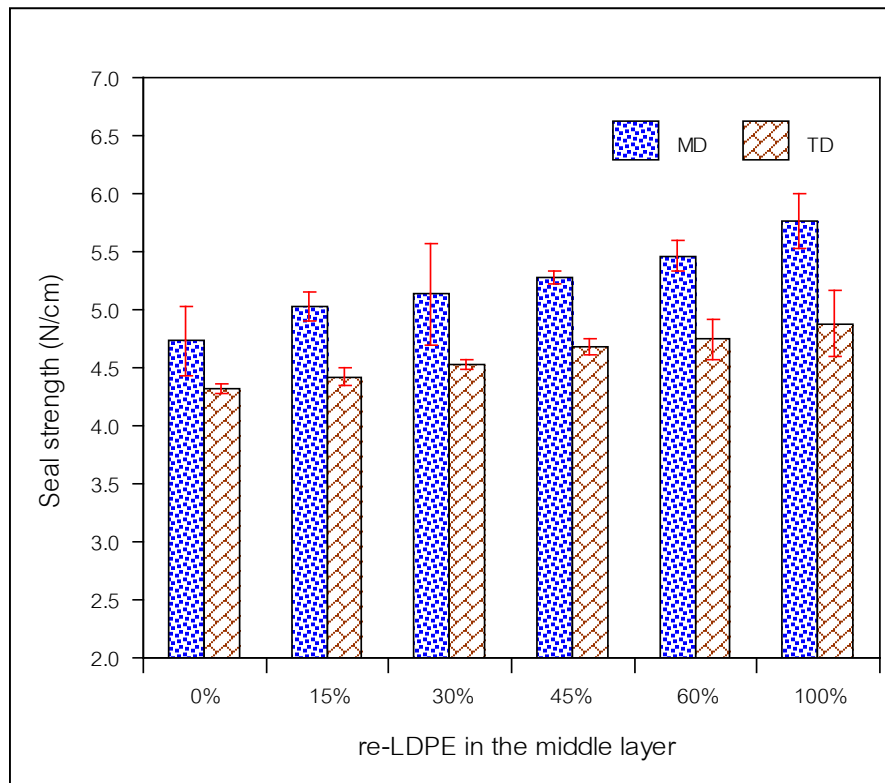
Figure 4.11 Seal strength of LDPE/LDPE-re-LDPE/LDPE films

4.2.5 Heat shrink property

The shrink ability is defined as the ratio of the differential length of a specimen after the maximum heat shrink ability compare to the original length of specimen. It is usually determined as shrinkage percent which can be expressed by the following equation.

$$\text{Shrinkage percent (\%)} = 100 \times (L_o - L_i) / L_o$$

where L_o = the original length of the specimen before heating

L_i = the length of specimen after fully shrank.
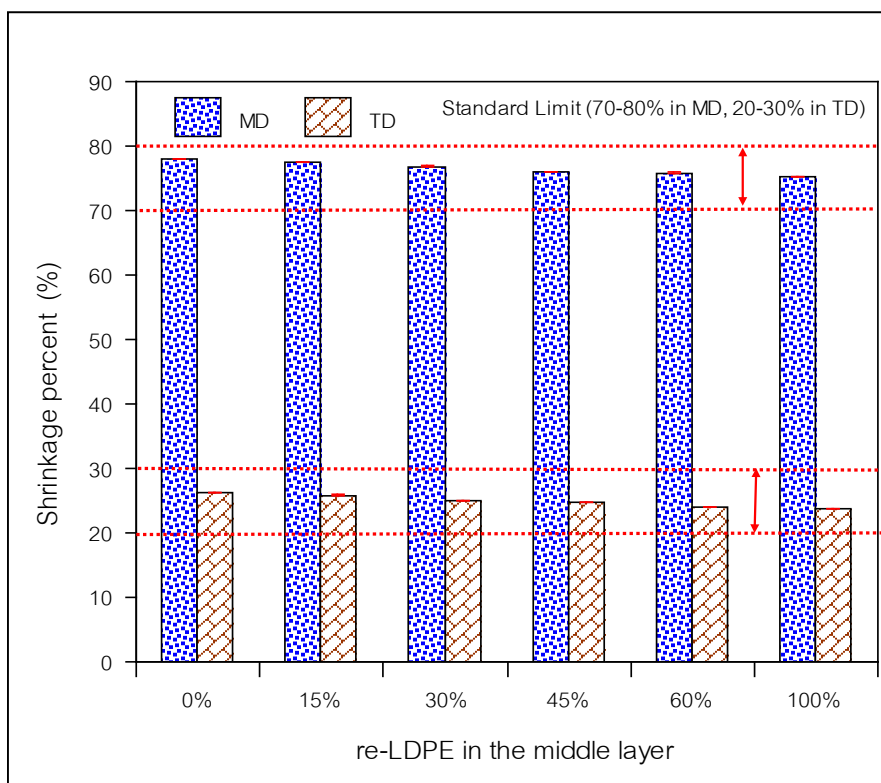
Figure 4.12 Shrinkage percent of LDPE/LDPE-re-LDPE/LDPE films

Figure 4.12 shows that the shrinkage percent slightly decreases from 77.90% to 75.32% in MD and 26.12% to 23.62% in TD with increasing re-LDPE content. All values are given in Appendix A (Table A17-18). MW reduction and a decrease in long side branches of re-LDPE after reprocessing induced the crystallization of the blends and strongly decreased the free volume of the polymer. This led to a decrease in shrink ability. However, the results indicate that three layered films obtained from all compositions of LDPE and re-LDPE blends even re-LDPE 100% can be used for shrink film applications in the soft drink markets since their shrinkage percents still remain in the normal commercial standards which are at 20-30% in TD and 70-80% in MD.

The results obtained from this section can be concluded that using re-LDPE 100 wt% in the middle layer not only improve the mechanical properties of the films both tensile properties and seal strength but also remain their heat shrink ability within the commercial standard. However, for an application in heavy duty products, good mechanical properties of the film are needed. Therefore, the next study is aimed to improve the mechanical properties of this film by blending with MDPE in the middle layer.

4.3 Characteristics and properties of LDPE/re-LDPE-MDPE/LDPE films

4.3.1 Film appearance

Figure 4.13 shows the appearance of three layered shrink film specimens having re-LDPE and MDPE blend in the middle layer while the outer layers compose only of virgin LDPE. These films are transparent and have the consistency in film width and thickness without gels, scratches or melt fractures. Haze and gloss properties of LDPE/re-LDPE-MDPE/LDPE films are shown in Figure 4.14. Higher density of MDPE gave the film exhibited increase in haze but did not significantly affect gloss of the films with increasing MDPE content in the middle layer. All values of haze and gloss are reported in Appendix A (Table A42, A46).
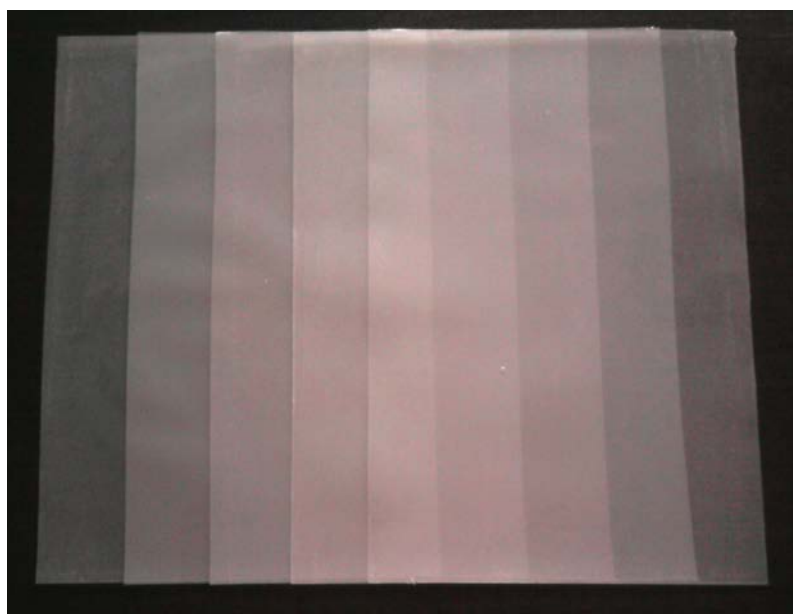
Figure 4.13 The appearance of LDPE/re-LDPE-MDPE/LDPE films
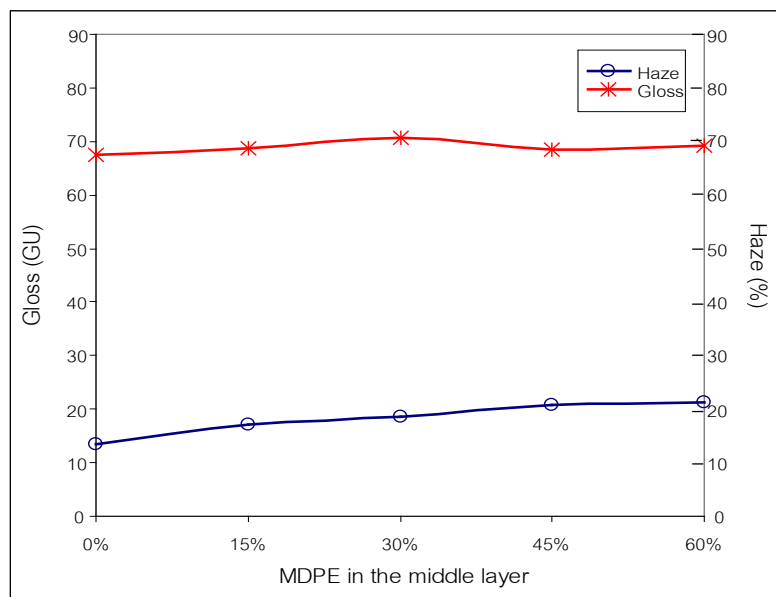
Figure 4.14 Haze and gloss of LDPE/re-LDPE-MDPE/LDPE films

4.3.2 Thermal behaviors

The results in Table 4.3 demonstrate that the melting temperatures (T_m) of all films did not significantly change with MDPE content. From DSC thermograms shown in Figure 4.15, it is clearly seen that the film containing 100 wt% of re-LDPE in the middle layer exhibits only a single sharp peak while all films containing re-LDPE and MDPE blends in the middle layer exhibit two separated peaks. One single crystallization peak forms during the cooling process indicating the existence of another type of crystal species. The difference in molecular structure between two kinds of polymer possess dissimilar crystallizing ability and crystallinity, which is responsible for phase separation in slowly cooling and show two distinct peaks [27]. %Crystallinity increases from 18% to 21% with increasing MDPE content from 0 to 60 wt%. It can be expected that the molecular structure of MDPE is more linearly and includes a few of short chain branches leading to a reduction of the entanglements among polymer molecules and increase %crystallinity as previously shown in Table 4.1. This provides the ability for molecular orientation into the direction of stretching and winding during the process and consequently increases % crystallinity of the films.

Table 4.3 Melting temperatures and % crystallinity of LDPE/re-LDPE-MDPE/LDPE films

re-LDPE:MDPE (wt%)	Melting Temperature T_1 (^{o}C)	Enthalpy ΔH_1 (J/g)	Melting Temperature T_2 (^{o}C)	Enthalpy ΔH_2 (J/g)	Crystallinity (%)
100:0	110	54	-	-	18
85:15	109	52	122	4	19
70:30	111	52	124	6	20
55:45	109	46	125	14	20
40:60	110	45	126	17	21
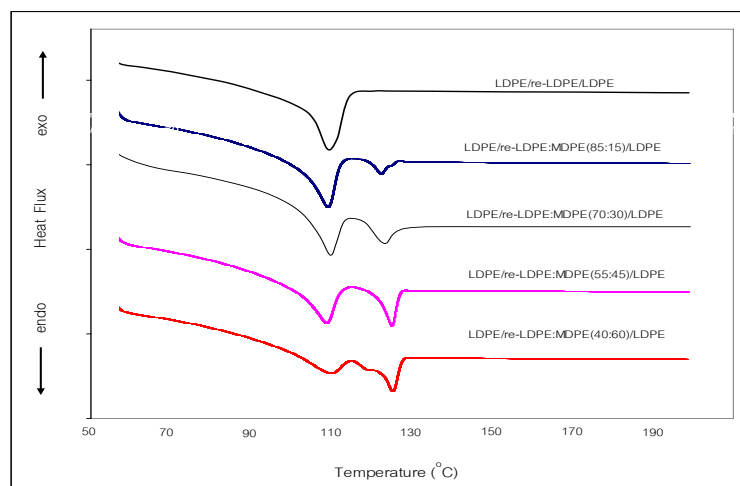
Figure 4.15 DSC thermograms of LDPE/re-LDPE-MDPE/LDPE films

4.3.3 Tensile properties

This experiment aims to study the property improvement of recycled three layered films by blending re-LDPE and MDPE in the middle layer. The tensile strength in both MD and TD of all LDPE/re-LDPE-MDPE/LDPE films are shown in Figure 4.16 and all values are given in Appendix A (Table A3-4). The results show that blending re-LDPE with MDPE in the middle layer improved tensile strength of the films. This may be caused by an increase in %crystallinity of these films. Figure 4.17 shows that %elongation at break in both direction increases with increasing MDPE content. This is because higher MW associated with

longer backbone chains of virgin MDPE compared to those of the recycled polymer can contribute to an increase in the molecular orientation and the percent of extension or %elongation at break in MD and TD. All values of %elongation at break are given in Appendix A (Table A27-28). Figure 4.18 shows that Young's modulus is highest when the amount of MDPE is 30 wt% and all values are given in Appendix A (Table A35-36). This suggests that at this amount, the crystallization effect of re-LDPE chains and the density effect of MDPE are dominate. However, as the amount of MDPE increased, Young's modulus decreased due to the ease in chain movement as previously described.
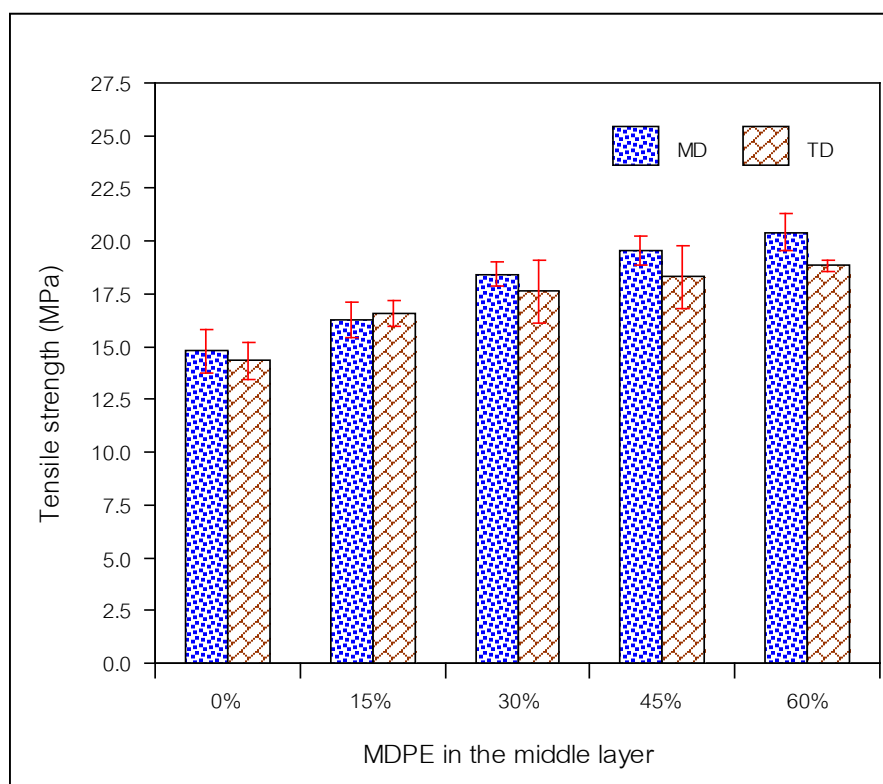
Figure 4.16 Tensile strength of LDPE/re-LDPE-MDPE/LDPE films
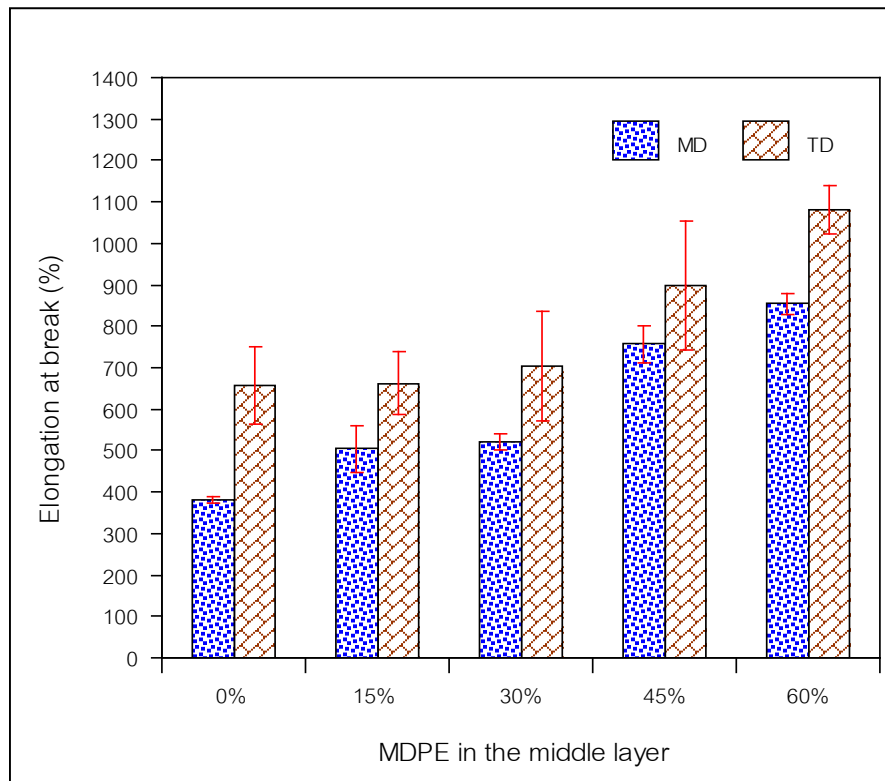
Figure 4.17 Elongation at break of LDPE/re-LDPE-MDPE/LDPE films
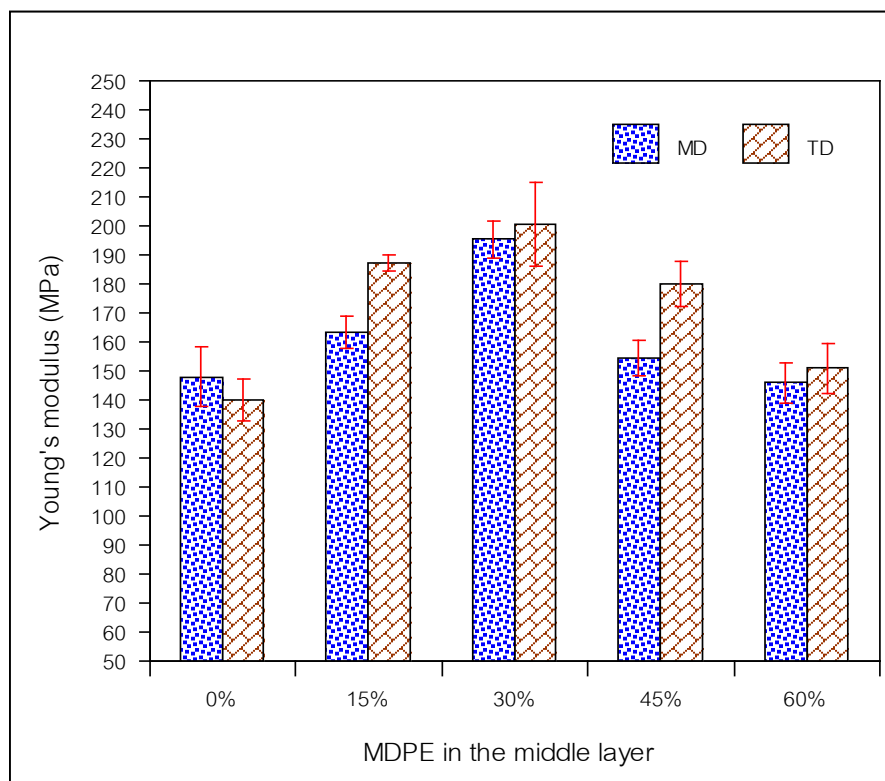
Figure 4.18 Young's modulus of LDPE/re-LDPE-MDPE/LDPE films.

4.3.4 Seal strength

Figure 4.19 shows three layered film of LDPE/re-LDPE-MDPE/LDPE specimen obtained from seal strength measurement having breaking point closed to heat seal region as same as previous experiment. From the results, seal strength is highest when MDPE content is 30 wt% as shown in Figure 4.20. Since heat seal ability is a function of polymer structure and sealing factors including heat seal temperature, pressure and given sufficient time. Therefore, as heat seal conditions were fixed; the molecular structure of polymer directly affects the seal property. Because MDPE structure is less branched than LDPE, this characteristic can improve heat distribution and the heat seal bonding between two surfaces with the optimum fraction of MDPE. However, at the highest content of MDPE 60 wt%, sealing strength decreases to 5.66 N/cm in MD and 4.59 N/cm in TD. These may be because MDPE has much higher melting point (T_m 131°C) than re-LDPE and LDPE (T_m 110-112 $^{\circ}$C); therefore, higher amount of MDPE needs higher thermal energy for melting. If heat seal temperature is insufficient, the polymer chains do not completely melt causing an ineffective sealing. All values of seal strength are given in Appendix A (Table A11-12).

Figure 4.19 Specimen of LDPE/re-LDPE-MDPE/LDPE film after seal strength measurement
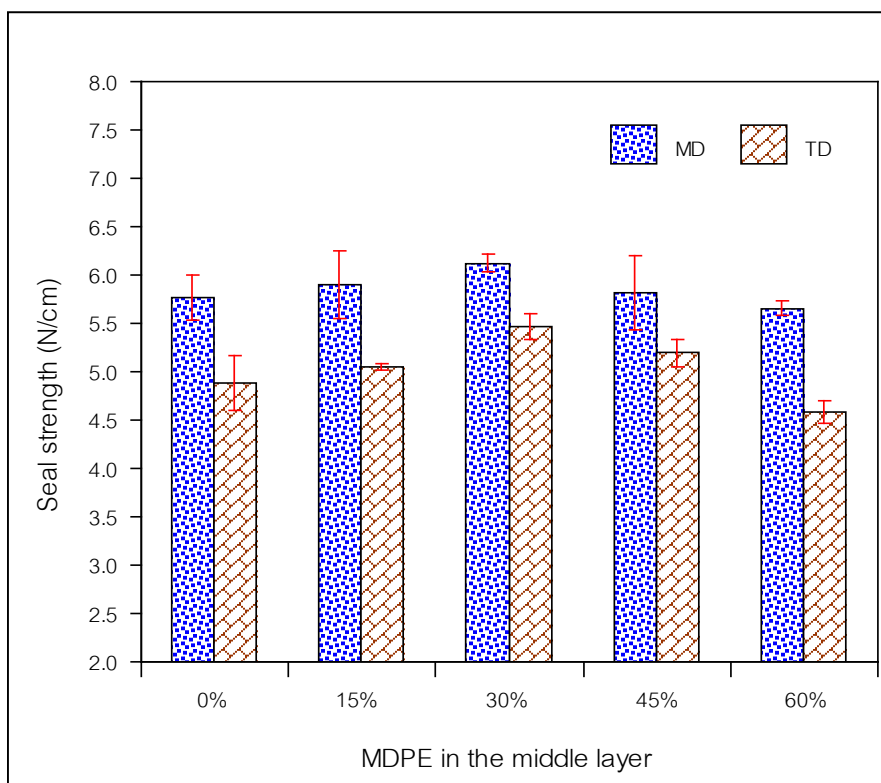
Figure 4.20 Seal strength of LDPE/re-LDPE-MDPE/LDPE films

4.3.5 Heat shrink property

Shrinkage percent of LDPE/re-LDPE:MDPE/LDPE films is shown in Figure 4.21. Increasing proportion of MDPE from 0 to 60 wt% reduces the shrink ability in both MD and TD. All values are given in Appendix A (Table A19-20). The results suggest that the films containing MDPE at 45 and 60 wt% cannot be used in shrink film application since their shrinkage percents fall below the commercial standards. Due to the linearity of MDPE structure and its few of side branches, MDPE chains can pack more closely and increase the density of the blend causing a reduction in the free volume of the polymer. As a result, shrink ability of the film decreases with increasing MDPE content.
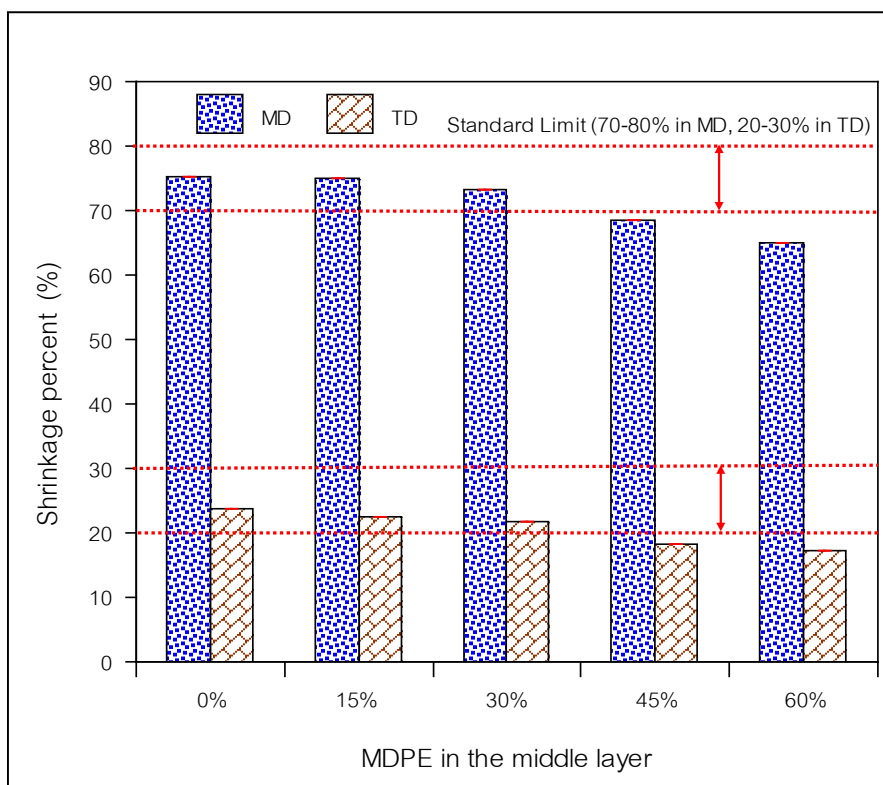
Figure 4.21 Shrinkage percent of LDPE/re-LDPE-MDPE/LDPE films

From the results, it can be seen that the mechanical properties of LDPE/re-LDPE/LDPE film can improve by blending with MDPE in the middle layer. It was found that the composition of re-LDPE-MDPE at 70:30 wt% gave the film that has highest seal strength, better tensile properties and exhibited the shrink ability within commercial standard for shrink film applications when compare with those of the film prepared using only re-LDPE in the middle layer and other compositions of MDPE blends. Therefore, the next experiment aimed to improve the seal strength properties of LDPE/re-LDPE-MDPE (70:30)/LDPE film by blending with LLDPE in the outer layers using for shrink film application of heavy duty product.

4.4 Characteristics and properties of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

4.4.1 Film appearance

Figure 4.22 shows the appearance of three layered shrink film specimens having re-LDPE and MDPE blend in the middle layer while the outer layers compose of LDPE and LLDPE blend. These films are tansparent and have the consistency in film width and thickness without gels, scratches or melt fractures. Haze and gloss properties of LDPE-LLDPE/ re-LDPE-MDPE/ LDPE-LLDPE films are shown in Figure 4.23. From the results, the increasing content of LLDPE in the outer layers has a good effect to enhance optical properties of the film by strongly decreasing haze and increasing gloss values due to the lower %crystallinity of LLDPE as previously shown in Table 4.1. All values of haze and gloss are reported in Appendix A (Table A43, A47).

Figure 4.22 The appearance of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films
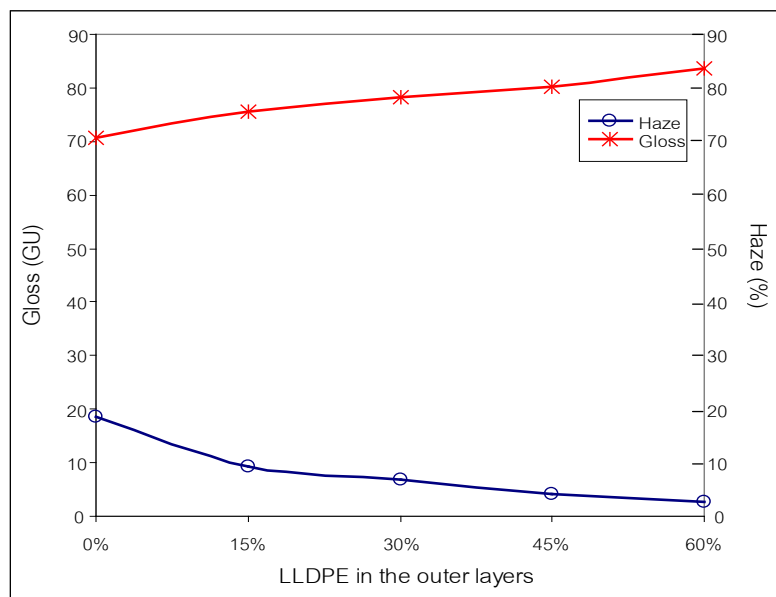
Figure 4.23 Haze and gloss of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

4.4.2 Thermal behaviors

The results in Table 4.4 demonstrate that blending LLDPE with LDPE did not significantly affect the melting temperatures of the films. However, DSC thermograms shown in Figure 4.24 suggest that the composed polymers are not perfectly compatible since three peaks are clearly observed as LLDPE content increases. In addition, increasing LLDPE content from 0 to 60 wt% decreases %crystallinity from 20% to 15%. This may be because LLDPE has much higher content of short chain branches and broad MW distribution; therefore, it can obstruct the molecular orientation and crystallization of LDPE.
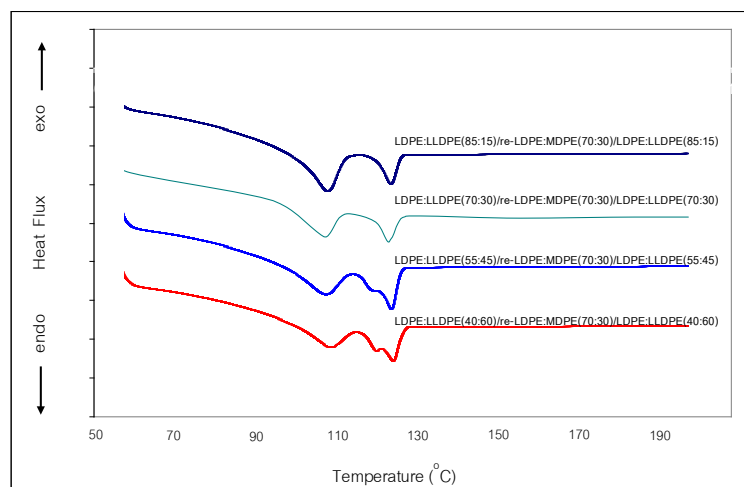
Figure 4.24 DSC thermograms of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

Table 4.4 Melting temperatures and % crystallinity of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

LDPE:LLDPE (wt%)	Melting Temperature T_1 (^{o}C)	Enthalpy ΔH_1 (J/g)	Melting Temperature T_2 (^{o}C)	Enthalpy ΔH_2 (J/g)	Crystallinity (%)
100:0	112	52	124	6	20
85:15	108	43	124	10	18
70:30	109	41	125	9	17
55:45	108	30	125	17	16
40:60	109	27	125	17	15

4.4.3 Tensile properties

It is clearly seen from Figure 4.25 that tensile strength slightly increases with increasing LLDPE content. All values of tensile strength are given in Appendix A (Table A5-6). This increasing may be due to the entanglement between LLDPE chains and intermolecular bonding between LLDPE and LDPE. However, this effect is not dominant; therefore, a decrease in %crystallinity plays an important role by increasing %elongation at break and decreasing Young's modulus with increasing LLDPE content as shown in Figures 4.26 and 4.27, respectively. All values of %elongation at break and Young's modulus are given in Appendix A (Table A29-30 and Table A37-38).
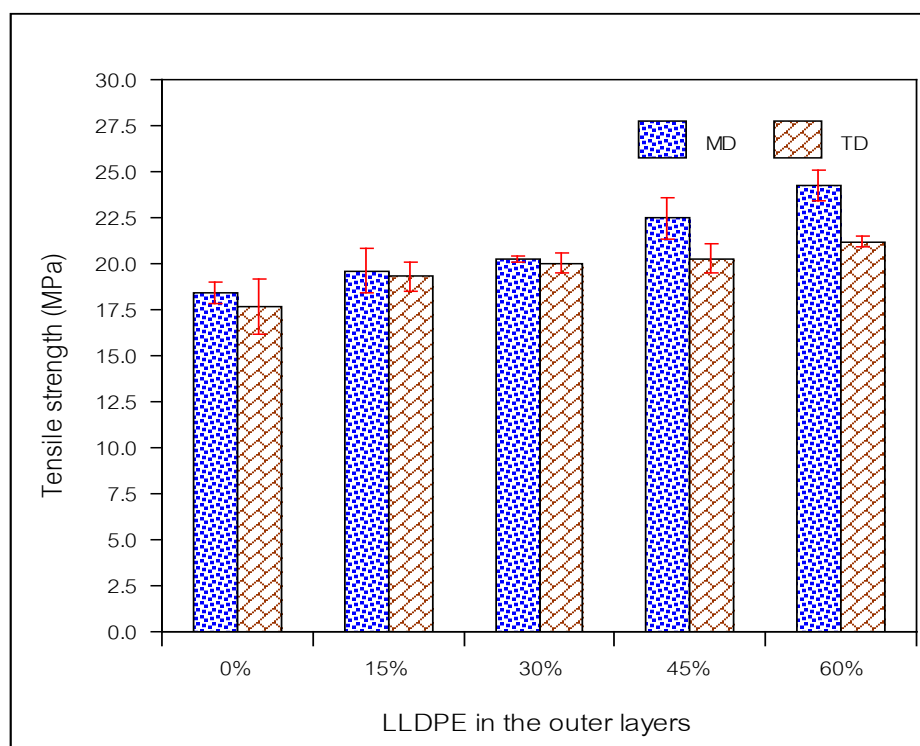
Figure 4.25 Tensile strength of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films
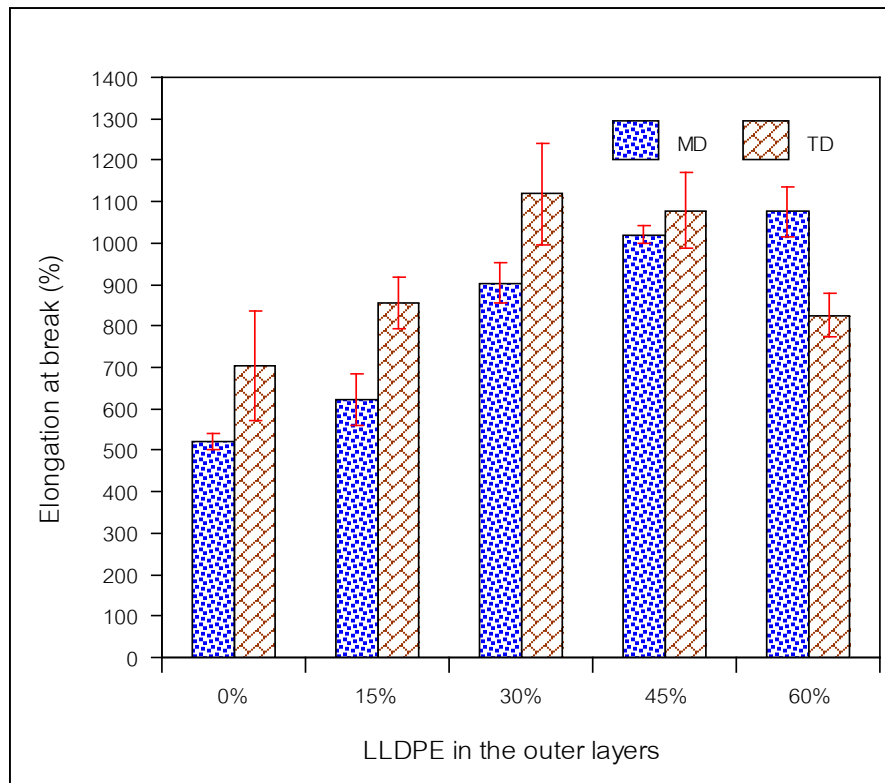
Figure 4.26 Elongation at break of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films
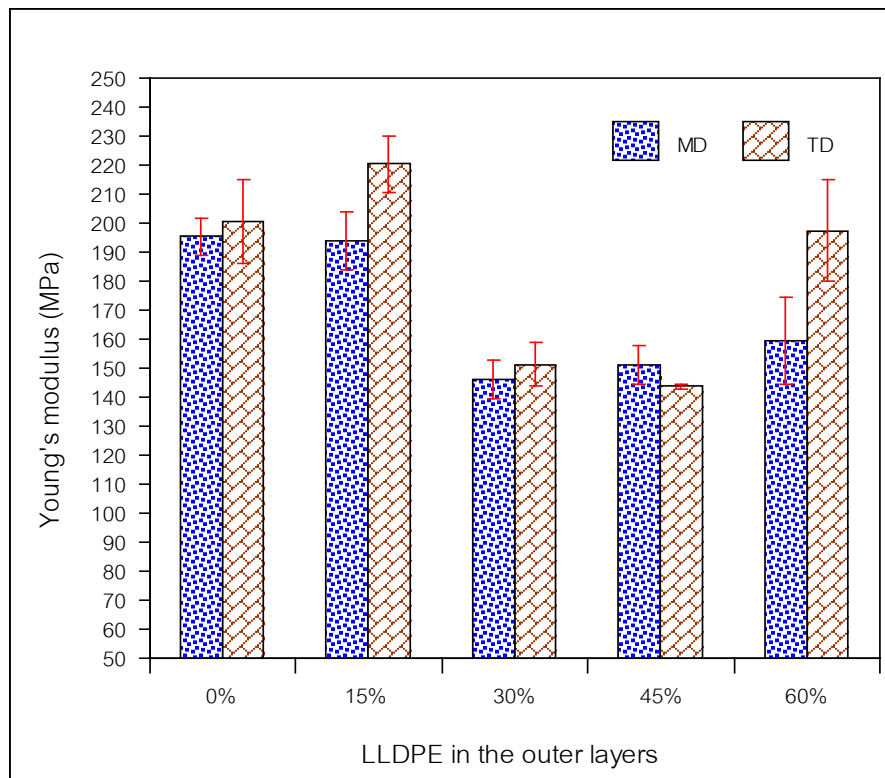
Figure 4.27 Young's modulus of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

4.4.4 Seal strength

Three layered film of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE specimen obtained from seal strength measurement having breaking point closed to heat seal region is shown in Figure 4.28. It can also be seen that the increasing LLDPE content increase seal strength of the films. The results show that when fixing the composition of re-LDPE:MDPE at 70:30 wt% in the middle layer and varying the proportions of LDPE-LLDPE in the outer layers, seal strength increases from 6.125 to 7.860 N/cm in MD and 5.464 to 5.840 N/cm in TD with increasing LLDPE contents from 0 to 30 wt% as shown in Figure 4.29. All values of seal strength are reported in Appendix A (Table A13-A14). These results can be explained that the large amounts of short chain branches and consistent molecular structure of LLDPE can contribute to better thermal distribution and regular melting after heating causing the increases in the ability of melting and diffusion of polymer molecules across two sealant layer interfaces and easy to generate the rearrangement after cooling due to the regular structure. However, when increasing LLDPE contents to 60 wt% seal strength has sharply decreased to 5.54 N/cm in MD and 4.676 N/cm in TD, respectively. This may be because LLDPE has higher melting point than re-LDPE and LDPE (122 $^{\circ}$C compare to 110 $^{\circ}$C). Therefore, at the higher content of LLDPE, it is necessary to increase the heat seal temperature in order to improve the ability of melting of LLDPE molecules.

Figure 4.28 Specimen of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE film after seal strength measurement
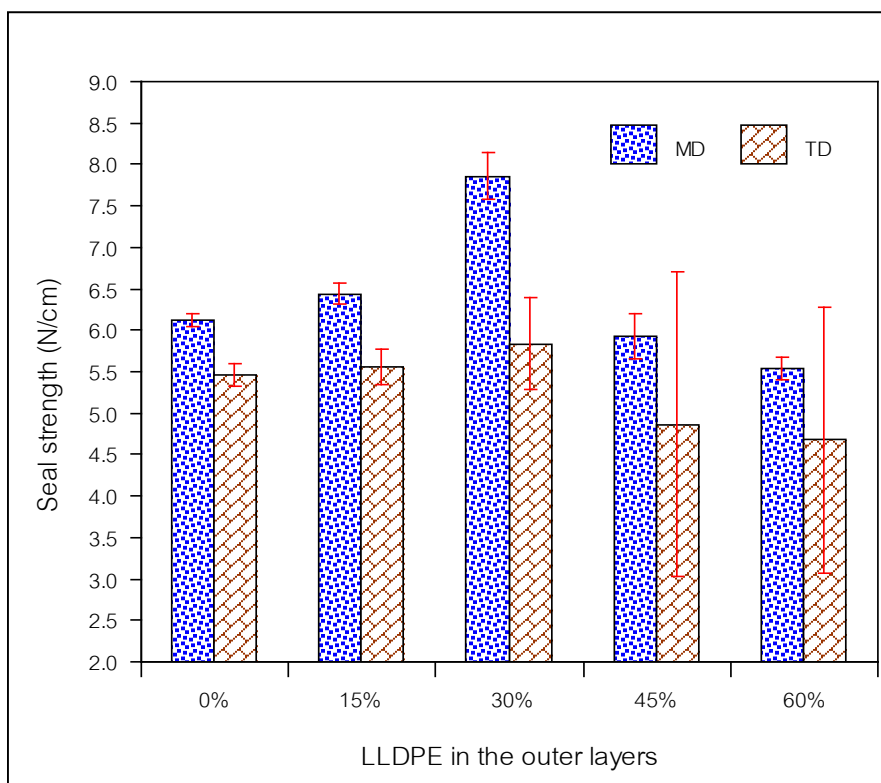
Figure 4.29 Seal strength of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

4.4.5 Heat shrink property

Figure 4.30 shows that the blended compositions of re-LDPE-MDPE and LDPE-LLDPE at the higher content of 45 and 60 wt% are not properly used for shrink film application since their shrinkage percents fall below commercial standard. However, it was found that the blended composition of re-LDPE:MDPE and LDPE:LLDPE at 15 and 30 wt% provided good mechanical properties and can be used for shrink film application especially in the soft drinks market because the shrinkage percents remain in normal standard. All values of shrinkage percent are reported in Appendix A (Table A21-A22).
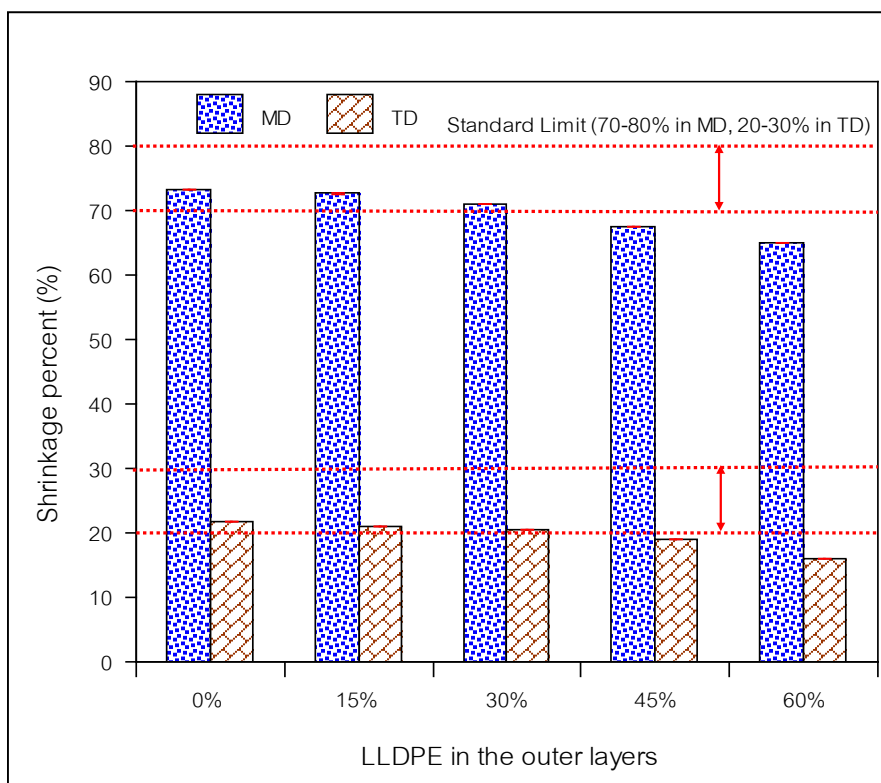
Figure 4.30 Shrinkage percent of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films

In this experiment, the results suggest that the highest seal strength property of LDPE/re-LDPE-MDPE/LDPE film can be achieved by blending the outer layers with LLDPE at the composition of 30 wt%. Moreover, this composition gave the film that has higher tensile property and exhibited the shrink ability within commercial standard for shrink film applications. The film obtained from this experiment has a possible to use for heavy duty product due to the mechanical properties improvement.

4.5 Characteristics and properties of LDPE/re-LDPE-CaCO$_3$/LDPE films

4.5.1 Film appearance

Figure 4.31 shows that LDPE/re-LDPE-CaCO$_3$/LDPE films are translucent and have the small amount of scratches on surface. It was also found that CaCO$_3$ strongly affected optical properties of the films by increasing haze but reducing gloss with increasing CaCO$_3$ content as shown in Figure 4.32. All values of haze and gloss are reported in appendix A (Table A44, A48). These results are discussed in relation to the higher density of CaCO$_3$ and the enhancement of %crystallinity causing a decrease in the transparency of the films [37]. Because of the changes in the optical properties, adding CaCO$_3$ at higher content into re-LDPE is limited.
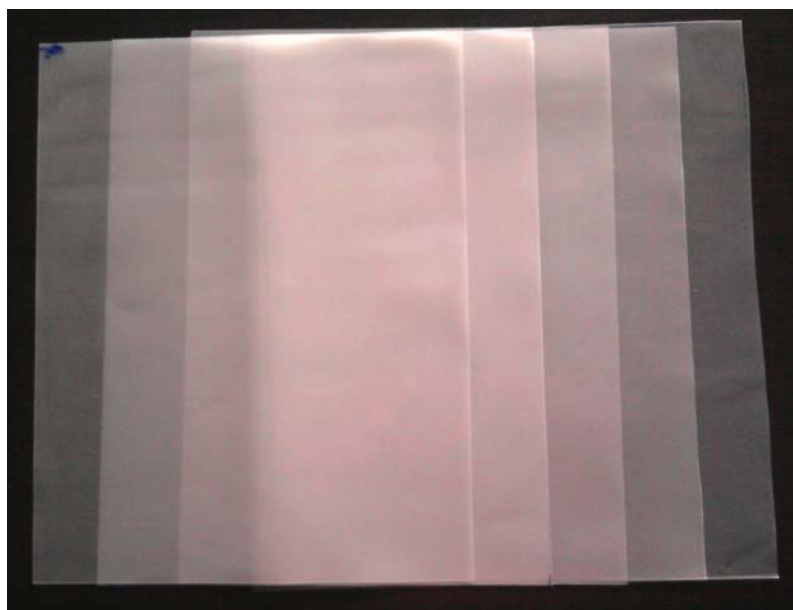
Figure 4.31 The appearance of LDPE/re-LDPE-CaCO$_3$/LDPE films
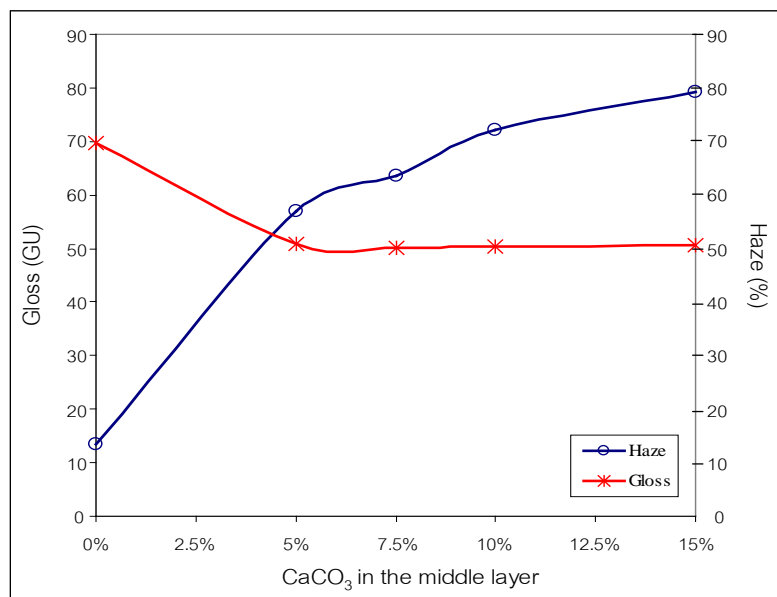
Figure 4.32 Haze and gloss of LDPE/re-LDPE-CaCO$_3$/LDPE films

4.5.2 Morphology analysis

SEM photographs of LDPE/re-LDPE-CaCO$_3$/LDPE films are shown in Figure 4.33. It can be seen the number of small CaCO$_3$ particles increased with increasing higher filler concentrations. The results demonstrated that CaCO$_3$ filler exhibited a good dispersion in re-LDPE matrix for all compositions. This may be because of the pretreated with stearic acid on CaCO$_3$ surface can reduce their surface energy and improve their dispersion in polymer. However, SEM micrographs also exhibit that the dispersion characteristic of CaCO$_3$ in re-LDPE matrix displayed a few of small agglomerate even if at the highest amount of CaCO$_3$ (15 wt%).

(a) 5 wt% CaCO$_3$ (500X)

(b) 7.5 wt% CaCO$_3$ (500X)

(c) 10 wt% CaCO$_3$ (500X)

(d) 15 wt% CaCO$_3$ (500X)

(a) 5 wt% CaCO$_3$ (1000X)

(b) 7.5 wt% CaCO$_3$ (1000X)

(c) 10 wt% CaCO$_3$ (1000X)

(d) 15 wt% CaCO$_3$ (1000X)
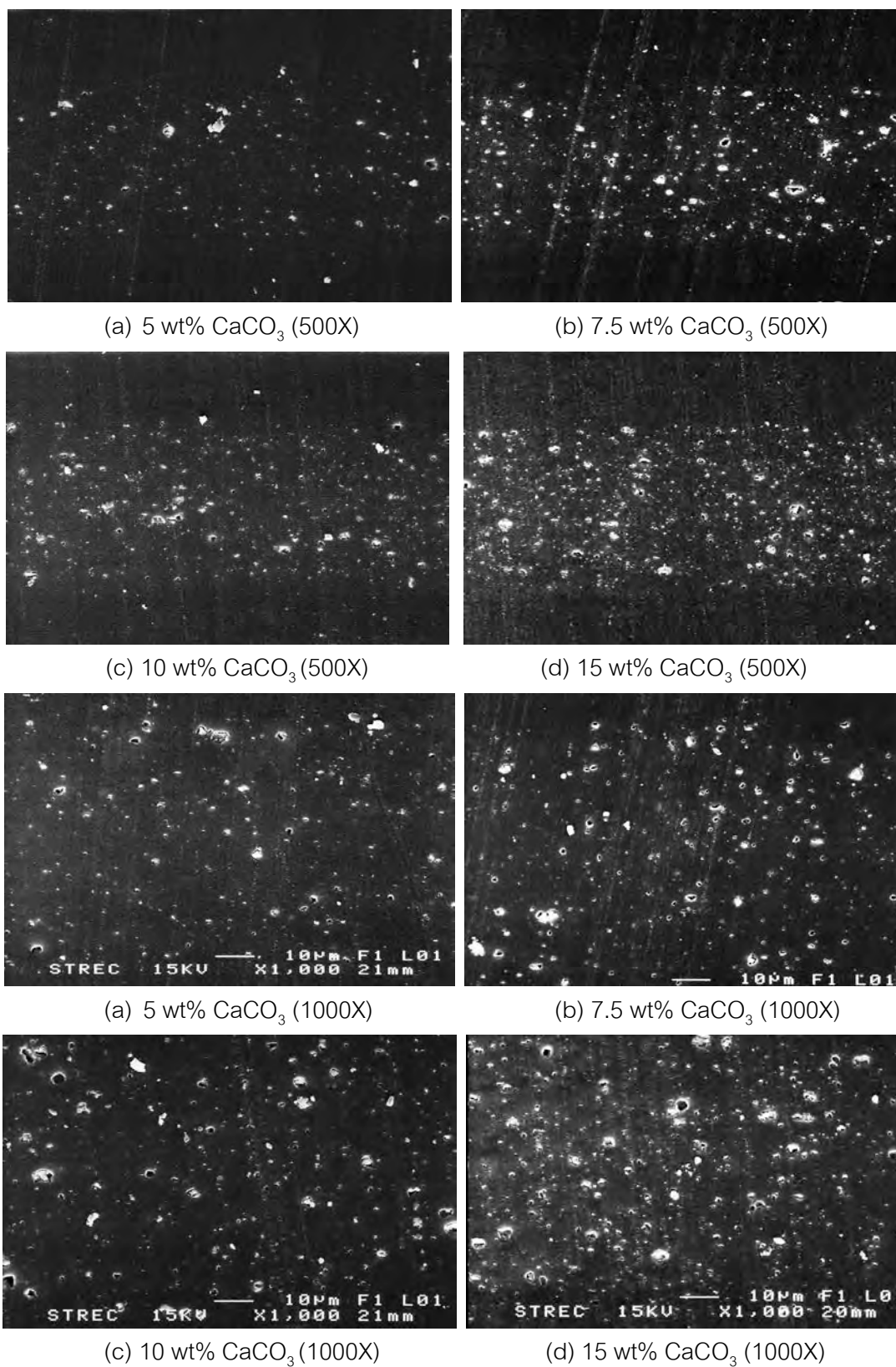
Figure 4.33 SEM micrographs of LDPE/re-LDPE-CaCO$_3$/LDPE films

4.5.3 Thermal behaviors

Figure 4.34 shows DSC thermograms of LDPE/re-LDPE-CaCO$_3$/LDPE films. It was found that DSC melting peaks of all compositions show a single sharp peak similar to those of LDPE/re-LDPE-CaCO$_3$/LDPE films. This suggests that adding CaCO$_3$ did not affect the melting temperature of the films. However, it can be seen from Table 4.5 that %crystallinity increases with increasing CaCO$_3$ amount. This may be because CaCO$_3$ probably acted as the nucleating agent in re-LDPE matrix. Moreover, a small particle size and treated surface of CaCO$_3$ corresponding with a good mixing system of co-extruder can contribute to improve the nucleation of PE crystallization and the interaction between two dispersion phases.
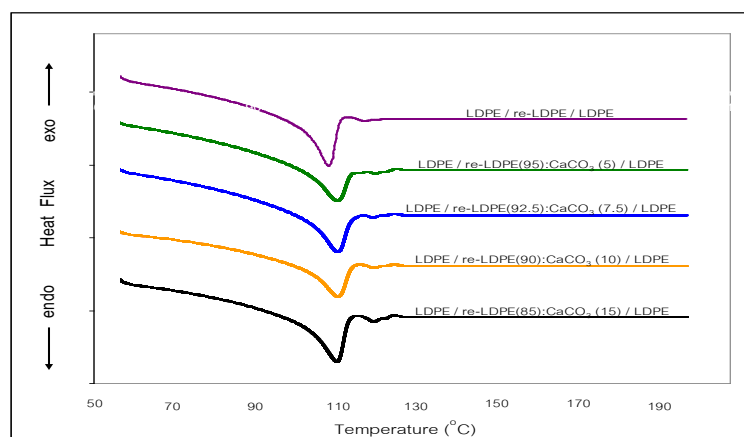
Figure 4.34 DSC thermograms of LDPE/re-LDPE-CaCO$_3$/LDPE films

Table 4.5 Melting temperatures and % crystallinity of LDPE/re-LDPE-CaCO$_3$/LDPE films

re-LDPE:CaCO$_3$ (wt%)	Melting Temperature T$_1$ (^{o}C)	Enthalpy ΔH$_1$ (J/g)	Crystallinity (%)
100:0	110	54	18
95:5	112	59	20
92.5:7.5	111	62	21
90:10	111	64	22
85:15	111	66	23

4.5.4 Tensile properties

It is clearly seen from Figure 4.35 that tensile strength of LDPE/re-LDPE-CaCO$_3$/LDPE films is higher that of unfilled film. This may be due to an increase in %crystallinity with increasing the filler content. However, %elongation at break is seemed not to be related with CaCO$_3$ content as shown in Figure 4.36 possibly because of some aggregated portions of CaCO$_3$ acting as defects in the films. On the other hand, Young's modulus of LDPE/re-LDPE-CaCO$_3$/LDPE films as shown in Figure 4.37 exhibits the same trend as tensile strength suggesting that the stiffness of the film increases with increasing CaCO$_3$ content. All values of tensile strength, %elongation at break and Young's modulus are reported in Appendix A (Table A7-A8, A31-32, A39-A40).
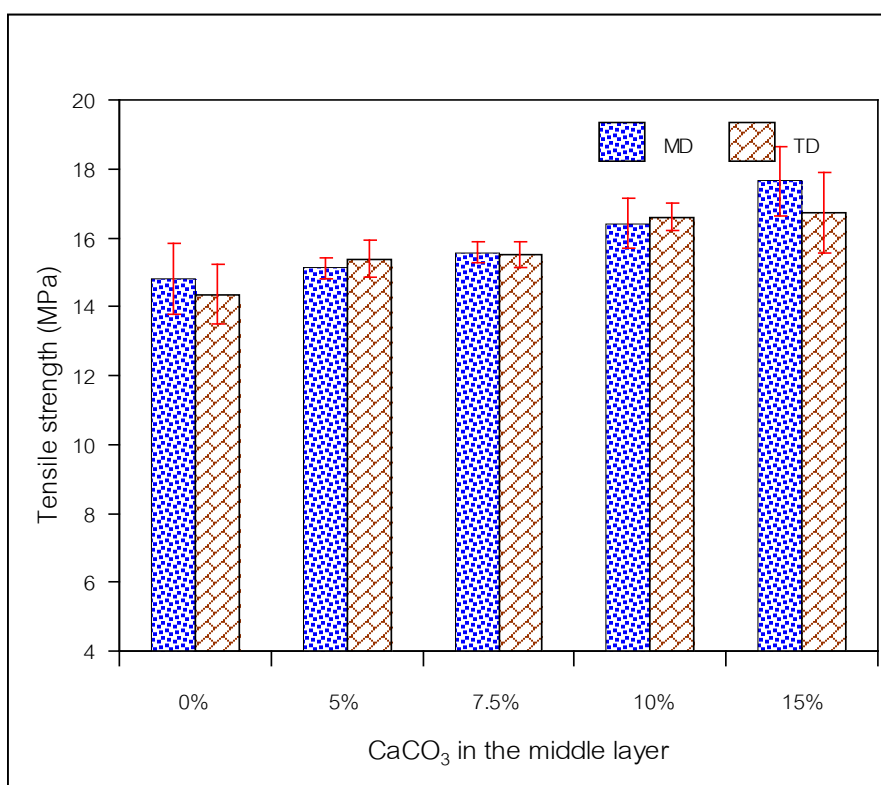
Figure 4.35 Tensile strength of LDPE/re-LDPE-CaCO$_3$/LDPE films
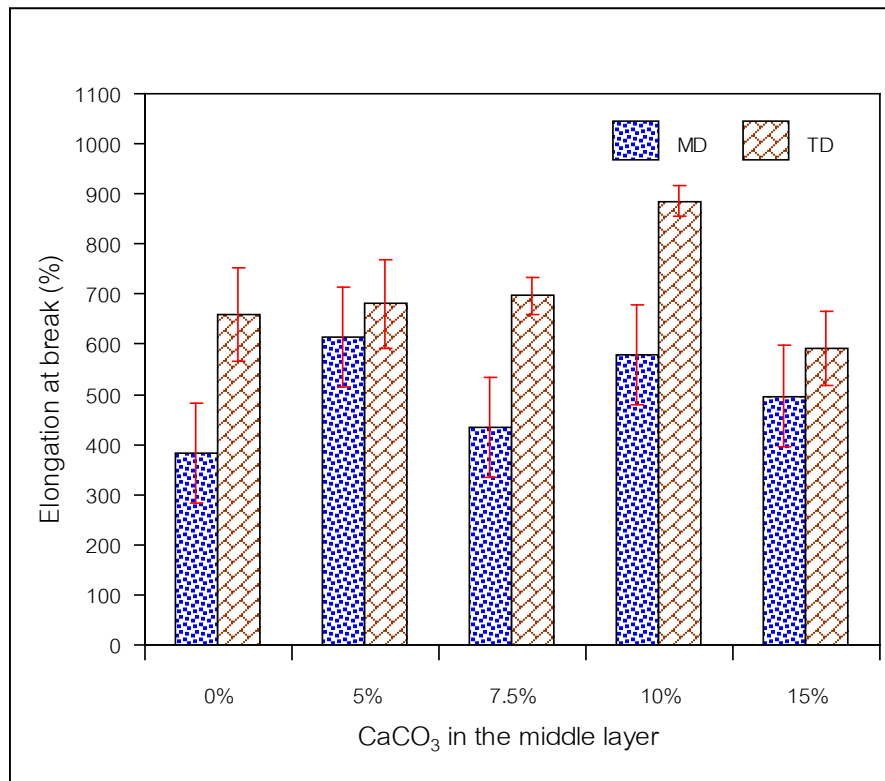
Figure 4.36 Elongation at break of LDPE/re-LDPE-CaCO$_3$/LDPE films
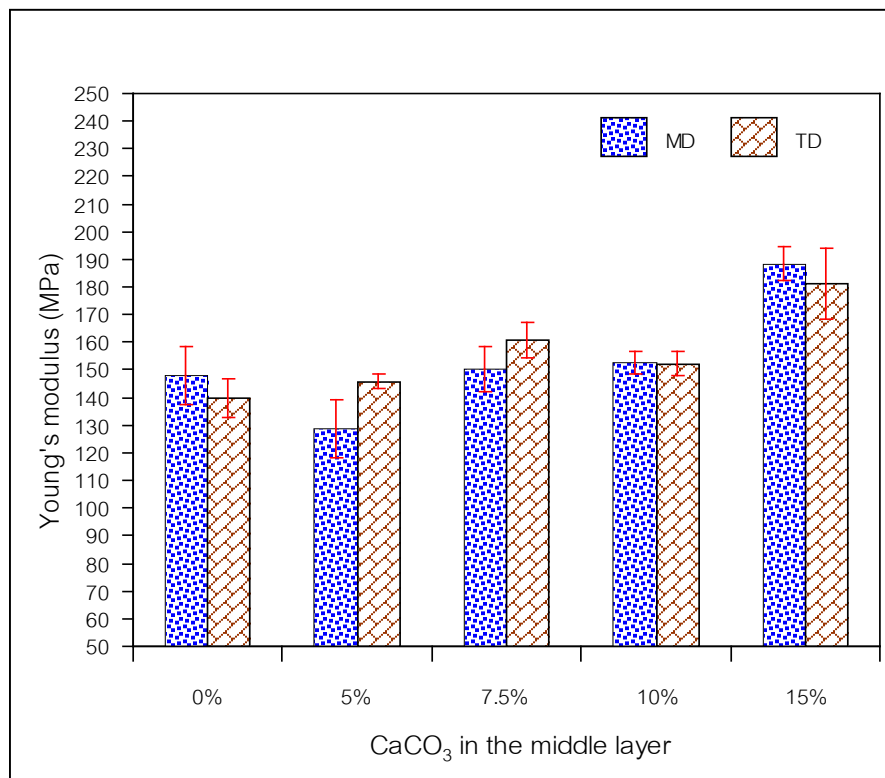
Figure 4.37 Young's modulus of LDPE/re-LDPE-CaCO$_3$/LDPE films

4.5.5 Seal strength

Figure 4.38 shows three layered film of LDPE/re-LDPE-CaCO$_3$/LDPE specimen obtained from seal strength measurement having breaking point closed to heat seal region. The results in Figure 4.39 show that adding CaCO$_3$ strongly increases seal strength. This may be because CaCO$_3$ has higher thermal conductivity than the polymer; therefore, the heat generating throughout the film under sealing condition is faster than without CaCO$_3$. Consequently, melting ability and polymer diffusion between two polymer interfaces are improved. However, too many rigid particles of CaCO$_3$ can contaminate among two sealant layer interfaces resulting in a slightly decrease in heat seal strength of the films with increasing the amount of CaCO$_3$ from 5 to 15 wt%. All values of seal strength are reported in Appendix A (Table A15-A16).

Figure 4.38 Specimen of LDPE/re-LDPE-CaCO$_3$/LDPE film after seal strength measurement
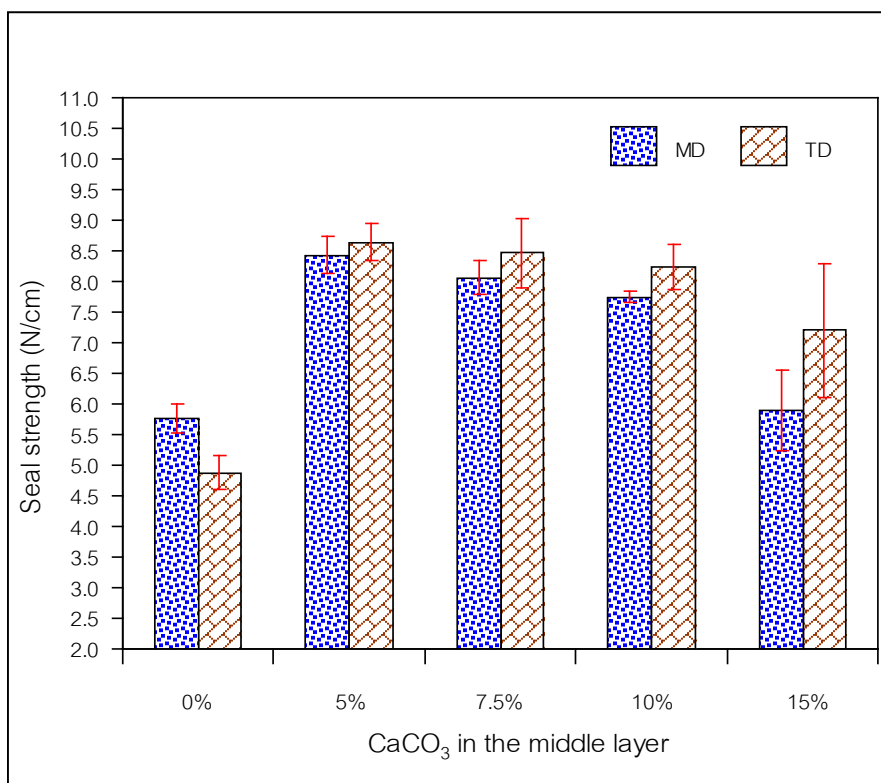
Figure 4.39 Seal strength of LDPE/re-LDPE-CaCO$_3$/LDPE films

4.5.6 Heat shrink property

Figure 4.40 shows that increasing CaCO$_3$ content increases shrinkage ratio of the films. All values of shrinkage percent are reported in Appendix A (Table A23-A24). Higher heat conductivity of CaCO$_3$ (2.4-3.0 W/K.m.) when compare to PE material (0.42-0.51 W/K.m.) significantly increases the temperature and the rate of heat transfer throughout the polymer matrix resulting in higher shrinkage tendency after immerging into hot oil bath. However, higher CaCO$_3$ content of 10 and 15 wt%, shrinkage percents of the films are over normal standard. These results suggest that the addition of CaCO$_3$ at 5 and 7.5 wt% offers high quality shrink film because they can improve the mechanical properties and shrink ability in normal standard which can be used for shrink film application.
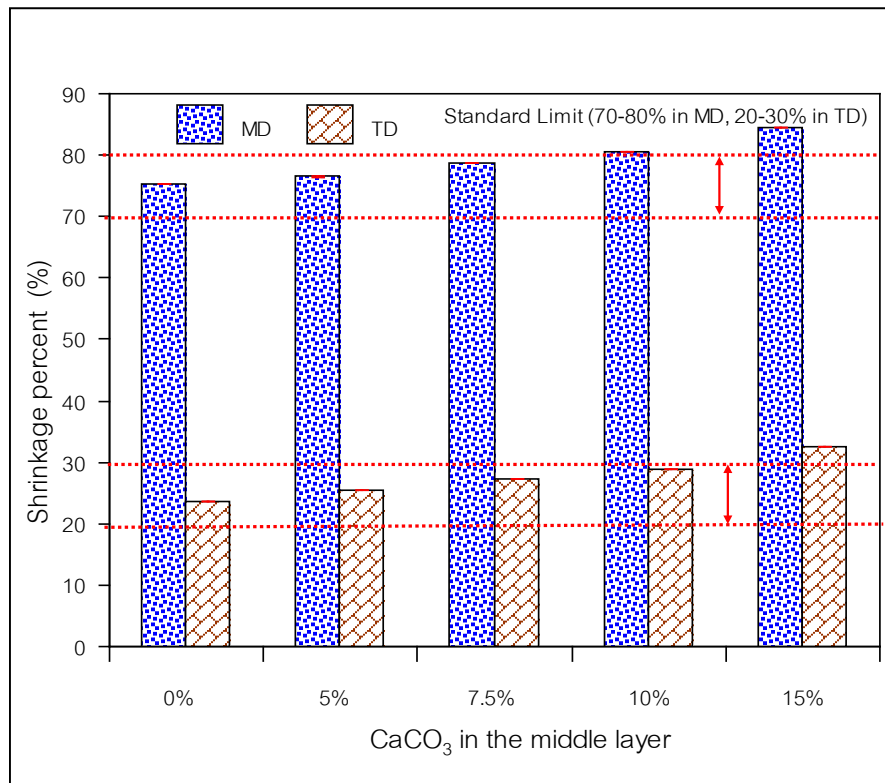
Figure 4.40 Shrinkage percent of LDPE/re-LDPE-CaCO$_3$/LDPE films

CHAPTER V

CONCLUSIONS

5.1 Conclusions

- Three layered shrink films having re-LDPE in the middle layer were prepared using blown film co-extrusion. The results showed that %crystallinity of the films increased with increasing re-LDPE content resulting in the improvement of tensile strength. Other properties including optical property, seal strength and heat shrink ability of these films were comparable with those of the film prepared using only virgin LDPE. This suggested that re-LDPE can be used as the middle layer of three layered shrink film instead of virgin LDPE.

- Due to higher molecular weight and longer backbone chains of MDPE compared to those of re-LDPE, it was found that tensile properties and seal strength of LDPE/re-LDPE-MDPE/LDPE films were better than those of LDPE/re-LDPE/LDPE film. However, too much MDPE content decreased optical property, seal strength and heat shrink ability of the films. The composition of re-LDPE-MDPE at 70:30 wt% gave the film that has highest seal strength property, better tensile strength and exhibited the shrink ability within commercial standard for shrink film applications.

- Large amounts of short chain branches and consistent molecular structure of LLDPE can contribute to the thermal distribution and regular melting after heating. As a result, seal strength of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE films strongly increased. Higher LLDPE content also improved optical properties by decreasing haze and increasing gloss of the films. However, too much LLDPE content decreased seal strength because it has much higher melting point than LDPE; therefore, it was more difficult to melt when MDPE content was increased. The composition of LDPE-LLDPE at 70:30 wt% in the outer layers should be used because the film gave highest seal strength, good tensile properties and exhibited heat shrink ability suitable for shrink film applications.

-   Adding calcium carbonate ($CaCO_3$) into re-LDPE middle layer also improved mechanical properties of LDPE/re-LDPE/LDPE film. SEM analysis revealed good dispersion of $CaCO_3$ in re-LDPE matrix which may be a result of surface treatment by stearic acid and its small particle size which was only 1 micron. Higher thermal conductivity of $CaCO_3$ also improved seal strength and strongly increased heat shrink ability of the films. However, adding too much $CaCO_3$ decreased the optical property and slightly decreased seal strength. The suitable amount of $CaCO_3$ to be added was 7.5 wt% because the film exhibited better tensile properties, much higher seal strength and better shrink ability than the film prepared without $CaCO_3$.

-   Finally, recycled three layered shrink film obtained from this experiment has a possible to use for shrink film applications. Moreover, this method is a good strategy that can be used to reduce of polyethylene film wastes, environmental friendly, good benefit and can also reduce the consumption of virgin LDPE.

5.2 Recommendation

-   The possibility of using re-LDPE in the outer layer and the mechanical properties improvement of recycled three layered shrink film using other fillers or thermoplastic resins should be studied.

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APPENDICES

APPENDIX A

Table A1: Tensile strength of LDPE/LDPE-re-LDPE/LDPE in MD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	12.50	12.77	13.28	13.45	13.13	13.03	0.385
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	13.28	13.58	13.79	13.46	12.06	13.24	0.683
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	13.32	13.86	13.17	13.20	13.42	13.40	0.280
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	14.22	13.93	13.06	13.67	12.74	13.52	0.612
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	14.14	14.27	13.52	14.28	14.27	14.09	0.329
6	LDPE (100)	re- LDPE (100)	LDPE (100)	15.89	15.86	13.79	14.55	13.87	14.79	1.033

Table A2: Tensile strength of LDPE/LDPE-re-LDPE/LDPE in TD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	11.58	11.45	10.51	10.49	12.13	11.23	0.717
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	10.51	10.76	12.89	10.53	12.58	11.45	1.178
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	11.83	11.54	12.17	12.87	13.39	12.36	0.7598
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	12.90	13.48	12.91	13.23	11.21	12.75	0.8948
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	14.35	13.32	14.22	14.14	14.09	14.02	0.406
6	LDPE (100)	re-LDPE (100)	LDPE (100)	15.86	14.16	13.52	14.12	14.12	14.35	0.881

Table A3: Tensile strength of LDPE/re-LDPE-MDPE/LDPE in MD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	15.89	15.86	13.79	14.55	13.87	14.79	1.033
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	17.00	17.16	16.43	15.61	15.19	16.28	0.858
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	18.36	18.51	17.60	18.41	19.29	18.44	0.600
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	18.74	18.94	19.80	20.15	20.25	19.58	0.697
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	20.84	19.33	19.75	20.99	21.25	20.43	0.841

Table A4: Tensile strength of LDPE/re-LDPE-MDPE/LDPE in TD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	15.86	14.16	13.52	14.12	14.12	14.35	0.881
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	16.33	17.12	15.63	17.04	16.71	16.57	0.611
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	15.67	18.37	16.77	19.55	17.83	17.64	1.488
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	18.24	16.04	18.03	19.73	19.55	18.32	1.482
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	18.72	18.46	19.21	18.83	18.99	18.84	0.283

Table A5: Tensile strength of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	18.36	18.51	17.60	18.41	19.29	18.44	0.600
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	17.55	20.07	20.67	20.38	19.43	19.62	1.245
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	20.30	20.10	20.31	20.51	20.11	20.27	0.169
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	22.71	20.64	23.37	22.30	23.40	22.48	1.129
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	24.50	24.32	25.33	23.11	23.97	24.25	0.810

Table A6: Tensile strength of LDPE-LLDPE /re-LDPE-MDPE/LDPE-LLDPE in TD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	15.67	18.37	16.77	19.55	17.83	17.64	1.488
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	19.67	19.90	18.55	18.36	20.04	19.30	0.790
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	19.98	19.61	19.44	20.72	20.40	20.03	0.535
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	19.70	20.47	21.58	19.74	19.90	20.28	0.788
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	21.40	21.07	20.90	21.60	21.06	21.21	0.284

Table A7: Tensile strength of LDPE/re-LDPE-CaCO$_3$/LDPE in MD

| No. | Film formulations (wt%) | | | Tensile strength (MPa) | | | | | | |
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	15.89	15.86	13.79	14.55	13.87	14.79	1.033
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	15.20	14.61	15.24	15.38	15.15	15.12	0.295
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	15.37	16.09	15.58	15.41	15.41	15.57	0.301
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	15.44	17.03	17.24	16.06	16.32	16.42	0.733
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	16.82	18.18	19.09	16.64	17.56	17.66	1.007

Table A8: Tensile strength of LDPE/re-LDPE-CaCO$_3$/LDPE in TD

No.	Film formulations (wt%)			Tensile strength (MPa)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	15.86	14.16	13.52	14.12	14.12	14.35	0.881
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	15.77	14.56	15.10	15.66	15.85	15.39	0.549
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	15.37	15.29	15.87	15.93	15.12	15.52	0.363
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	17.22	16.42	16.21	16.38	16.72	16.59	0.399
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	17.32	15.52	15.39	17.87	17.46	16.71	1.165

Table A9: Seal strength of LDPE/LDPE-re-LDPE/LDPE in MD

No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	4.871	4.332	4.920	4.498	5.037	4.731	0.301
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	5.200	4.960	5.020	4.860	5.080	5.024	0.128
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	5.469	5.254	5.546	4.493	4.908	5.134	0.435
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	5.248	5.206	5.347	5.294	5.287	5.277	0.053
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	5.512	5.374	5.337	5.426	5.663	5.462	0.130
6	LDPE (100)	re- LDPE (100)	LDPE (100)	5.717	5.625	5.503	6.128	5.850	5.764	0.239

Table A10: Seal strength of LDPE/LDPE-re-LDPE/LDPE in TD

| No. | Film formulations (wt%) | | | Seal strength (N/cm) | | | | | | |
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	4.286	4.393	4.305	4.312	4.331	4.326	0.041
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	4.488	4.480	4.322	4.350	4.473	4.423	0.080
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	4.505	4.588	4.541	4.546	4.462	4.528	0.047
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	4.606	4.641	4.762	4.636	4.739	4.677	0.069
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	4.719	4.636	4.568	5.024	4.782	4.746	0.176
6	LDPE (100)	re-LDPE (100)	LDPE (100)	4.731	4.623	5.199	5.115	4.722	4.878	0.285

Table A11: Seal strength of LDPE/re-LDPE-MDPE/LDPE in MD

No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	5.717	5.625	5.503	6.128	5.850	5.764	0.239
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	5.339	6.007	5.930	6.280	5.941	5.899	0.344
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	6.253	6.148	6.084	6.112	6.028	6.125	0.084
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	6.185	6.266	5.556	5.675	5.400	5.817	0.387
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	5.569	5.667	5.621	5.669	5.764	5.658	0.072

Table A12: Seal strength of LDPE/re-LDPE-MDPE/LDPE in TD

No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	4.731	4.623	5.199	5.115	4.722	4.878	0.285
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	5.020	5.023	5.100	5.066	5.040	5.050	0.033
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	5.560	5.242	5.477	5.580	5.458	5.464	0.134
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	5.326	5.098	5.069	5.109	5.380	5.196	0.145
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	4.606	4.722	4.404	4.540	4.655	4.585	0.121

Table A13: Seal strength of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD

No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	6.253	6.148	6.084	6.112	6.028	6.125	0.084
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	6.462	6.272	6.582	6.550	6.346	6.442	0.132
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	7.785	8.231	7.489	8.057	7.745	7.861	0.289
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	6.373	5.995	5.877	5.716	5.699	5.932	0.275
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	5.549	5.575	5.681	5.316	5.581	5.540	0.135

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Table A14: Seal strength of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in TD

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No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	5.560	5.242	5.477	5.580	5.458	5.464	0.134
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	5.323	5.668	5.428	5.503	5.858	5.556	0.210
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	6.682	5.546	5.332	5.521	6.119	5.840	0.556
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	4.300	4.855	5.207	5.126	4.838	4.865	1.831
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	4.563	4.328	4.017	5.244	5.227	4.676	1.609

Table A15: Seal strength of LDPE/re-LDPE-CaCO$_3$/LDPE in MD

No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	5.717	5.625	5.503	6.128	5.850	5.764	0.239
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	8.018	8.177	8.197	8.198	8.251	8.432	0.313
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	7.770	7.778	7.815	7.849	7.873	8.064	0.272
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	7.622	7.655	7.666	7.731	7.751	7.750	0.088
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	4.427	5.315	5.717	5.802	5.840	5.889	0.662

<p align="center">Table A16: Seal strength of LDPE/re-LDPE-CaCO$_3$/LDPE in TD</p>

No.	Film formulations (wt%)			Seal strength (N/cm)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	4.731	4.623	5.199	5.115	4.722	4.878	0.285
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	8.244	8.248	8.264	8.387	8.466	8.640	0.301
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	7.760	7.976	7.976	8.099	8.434	8.461	0.576
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	7.720	7.739	7.886	8.138	8.218	8.239	0.372
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	5.709	5.858	6.557	6.584	6.763	7.200	1.099

Table A17: Shrink ratio of LDPE/LDPE-re-LDPE/LDPE in MD

| No. | Film formulations (wt%) | | | Dimension (cm) | | | | | | | Shrink ratio (%) |
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	LDPE (100)	LDPE (100)	2.23	2.19	2.17	2.22	2.24	2.21	0.029	77.90
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	2.28	2.25	2.27	2.29	2.23	2.26	0.024	77.36
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	2.34	2.28	2.29	2.33	2.32	2.31	0.026	76.88
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	2.38	2.37	2.40	2.41	2.38	2.39	0.016	76.12
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	2.42	2.40	2.43	2.39	2.41	2.41	0.016	75.90
6	LDPE (100)	re-LDPE (100)	LDPE (100)	2.48	2.44	2.48	2.46	2.48	2.47	0.018	75.32

Table A18: Shrink ratio of LDPE/LDPE-re-LDPE/LDPE in TD

No.	Film formulations (wt%)			Dimension (cm)							Shrink ratio (%)
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	LDPE (100)	LDPE (100)	7.40	7.35	7.38	7.40	7.41	7.39	0.024	26.12
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	7.42	7.43	7.43	7.40	7.39	7.41	0.018	25.86
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	7.49	7.47	7.49	7.48	7.50	7.49	0.011	25.14
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	7.55	7.53	7.51	7.50	7.54	7.53	0.021	24.74
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	7.60	7.58	7.56	7.59	7.61	7.59	0.019	24.12
6	LDPE (100)	re-LDPE (100)	LDPE (100)	7.64	7.64	7.61	7.65	7.65	7.64	0.016	23.62

Table A19: Shrink ratio of LDPE/re-LDPE-MDPE/LDPE in MD

No.	Film formulations (wt%)			Dimension (cm)							Shrink ratio (%)
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	re-LDPE (100)	LDPE (100)	2.48	2.44	2.48	2.46	2.48	2.47	0.018	75.32
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	2.53	2.54	2.51	2.49	2.52	2.52	0.019	74.82
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	2.65	2.69	2.67	2.66	2.71	2.68	0.024	73.24
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	3.12	3.13	3.16	3.14	3.18	3.15	0.024	68.54
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	3.51	3.54	3.50	3.51	3.49	3.51	0.019	64.90

Table A 20: Shrink ratio of LDPE/re-LDPE-MDPE/LDPE in TD

No.	Film formulations (wt%)			Dimension (cm)							Shrink ratio (%)
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	re-LDPE (100)	LDPE (100)	7.64	7.64	7.61	7.65	7.65	7.64	0.016	23.62
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	7.77	7.75\	7.74	7.77	7.75	7.76	0.015	22.43
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	7.85	7.84	7.82	7.81	7.84	7.83	0.016	21.68
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	8.16	8.17	8.19	8.18	8.15	8.17	0.016	18.30
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	8.31	8.22	8.27	8.31	8.25	8.27	0.039	17.28

Table A 21: Shrink ratio of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD

| No. | Film formulations (wt%) | | | Dimension (cm) | | | | | | | shrink ratio (%) |
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	2.65	2.69	2.67	2.66	2.71	2.68	0.024	73.24
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	2.75	2.73	2.75	2.71	2.72	2.73	0.018	72.68
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	2.91	2.93	2.89	2.88	2.92	2.91	0.021	70.94
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	3.25	3.24	3.23	3.28	3.26	3.25	0.019	67.48
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	3.50	3.51	3.52	3.48	3.47	3.50	0.021	65.04

Table A22: Shrink ratio of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in TD

| No. | Film formulations (wt%) | | | Dimension (cm) | | | | | | | shrink ratio (%) |
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	7.85	7.84	7.82	7.81	7.84	7.83	0.016	21.68
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	7.91	7.92	7.88	7.86	7.89	7.89	0.024	21.08
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	7.94	7.96	7.93	7.93	7.97	7.95	0.018	20.54
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	8.12	8.13	8.08	8.08	8.09	8.10	0.023	19.00
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	8.40	8.41	8.38	8.37	8.42	8.40	0.021	16.04

Table A23: Shrink ratio of LDPE/re-LDPE-$CaCO_3$/LDPE in MD

No.	Film formulations (wt%)			Dimension (cm)							Shrink ratio (%)
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	re-LDPE (100)	LDPE (100)	2.48	2.44	2.48	2.46	2.48	2.47	0.018	75.32
2	LDPE (100)	re-LDPE : $CaCO_3$ (95:5)	LDPE (100)	2.30	2.40	2.35	2.35	2.40	2.36	0.042	76.40
3	LDPE (100)	re-LDPE : $CaCO_3$ (92.5:7.5)	LDPE (100)	2.15	2.15	2.14	2.15	2.13	2.14	0.009	78.56
4	LDPE (100)	re-LDPE : $CaCO_3$ (90:10)	LDPE (100)	1.91	1.95	1.96	1.97	1.93	1.94	0.024	80.56
5	LDPE (100)	re-LDPE : $CaCO_3$ (85:15)	LDPE (100)	1.55	1.50	1.60	1.60	1.55	1.56	0.042	84.40

Table A24: Shrink ratio of LDPE/re-LDPE-CaCO$_3$/LDPE in TD

No.	Film formulations (wt%)			Dimension (cm)							Shrink ratio (%)
	Outer	Middle	Outer	1	2	3	4	5	X	STD	
1	LDPE (100)	re-LDPE (100)	LDPE (100)	7.64	7.64	7.61	7.65	7.65	7.64	0.016	23.62
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	7.40	7.45	7.50	7.45	7.40	7.44	0.042	25.60
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	7.30	7.25	7.25	7.25	7.30	7.27	0.027	27.30
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	7.10	7.10	7.15	7.10	7.15	7.12	0.027	28.80
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	6.75	6.70	6.75	6.80	6.78	6.76	0.038	32.44

Table A25: Elongation at break of LDPE/LDPE-re-LDPE/LDPE in MD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	408	420	441	443	429	428	14.570
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	475	483	462	449	415	457	26.807
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	462	506	466	516	524	495	28.971
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	496	435	449	480	421	456	31.212
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	558	552	461	509	527	521	38.923
6	LDPE (100)	re-LDPE (100)	LDPE (100)	392	389	382	372	374	382	8.846

Table A26: Elongation at break of LDPE/LDPE-re-LDPE/LDPE in TD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	544	545	262	548	293	438	147.181
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	507	525	552	551	279	483	115.419
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	533	527	542	560	618	556	36.708
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	549	598	535	612	497	558	47.110
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	622	500	630	666	639	612	64.390
6	LDPE (100)	re-LDPE (100)	LDPE (100)	822	647	607	609	606	658	93.249

Table A27: Elongation at break of LDPE/re-LDPE-MDPE/LDPE in MD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	392	389	382	372	374	382	8.846
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	510	507	576	514	418	505	56.379
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	516	543	509	495	543	521	20.970
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	746	788	695	812	749	758	44.994
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	863	817	887	852	857	855	25.528

Table A28: Elongation at break of LDPE/re-LDPE-MDPE/LDPE in TD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	822	647	607	609	606	658	93.249
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	598	707	570	689	747	662	75.147
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	571	768	611	899	662	702	132.371
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	851	701	943	1070	922	898	155.377
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	1073	1040	1180	1040	1073	1081	57.560

Table A29: Elongation at break of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	516	543	509	495	543	521	20.970
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	564	703	663	567	614	622	60.605
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	882	843	908	916	972	904	47.000
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	1034	991	1049	1012	1015	1020	22.101
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	1069	1001	1075	1064	1171	1076	60.888

Table A30: Elongation at break of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in TD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	571	768	611	899	662	702	132.371
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	899	888	857	745	887	855	63.617
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	1177	1215	1108	1185	910	1119	123.278
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	1111	1130	1161	928	1061	1078	91.348
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	760	829	813	906	819	826	52.149

Table A31: Elongation at break of LDPE/re-LDPE-CaCO$_3$/LDPE in MD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	392	389	382	372	374	382	8.846
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	700	575	631	583	586	615	52.256
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	407	419	480	420	440	433	28.668
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	498	599	616	544	641	580	58.077
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	515	497	532	462	479	497	27.826

Table A32: Elongation at break of LDPE/re-LDPE-CaCO$_3$/LDPE in TD

No.	Film formulations (wt%)			Elongation at break (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	822	647	607	609	606	658	93.249
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	663	579	627	738	799	681	87.832
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	747	712	659	702	665	697	36.094
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	904	876	862	856	929	886	30.685
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	668	571	547	669	504	592	74.123

Table A33: Young's modulus of LDPE/LDPE-re-LDPE/LDPE in MD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	151	141	157	161	154	153	7.808
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	145	155	151	157	141	150	6.702
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	135	135	149	128	126	135	9.043
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	139	141	138	134	137	138	2.529
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	130	137	132	136	130	133	3.471
6	LDPE (100)	re-LDPE (100)	LDPE (100)	155	162	140	138	145	148	10.355

Table A34: Young's modulus of LDPE/LDPE-re-LDPE/LDPE in TD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	150	160	162	158	156	157	4.391
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	137	134	140	148	145	141	5.828
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	160	156	161	145	157	156	6.470
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	142	141	148	143	143	143	2.694
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	164	160	148	150	140	152	9.406
6	LDPE (100)	re-LDPE (100)	LDPE (100)	140	128	141	145	145	140	7.137

Table A35: Young's modulus of LDPE/re-LDPE-MDPE/LDPE in MD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	155	162	140	138	145	148	10.355
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	163	172	161	157	165	163	5.541
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	199	194	187	204	193	195	6.390
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	145	156	159	154	160	155	6.120
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	145	149	134	150	151	146	6.921

Table A36: Young's modulus of LDPE/re-LDPE-MDPE/LDPE in TD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	140	128	141	145	145	140	7.137
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	190	184	186	190	185	187	2.768
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	223	204	198	183	196	201	14.486
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	172	184	172	166	205	180	7.729
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	159	155	137	154	150	151	8.437

Table A37: Young's modulus of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	199	194	187	204	193	195	6.390
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	183	188	199	208	192	194	9.870
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	147	150	155	140	139	146	6.479
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	149	141	152	158	156	151	6.621
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	164	180	164	149	141	160	15.095

Table A38: Young's modulus of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in TD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	223	204	198	183	196	201	14.486
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	222	232	226	207	216	220	9.664
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	149	152	164	144	148	151	7.301
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	144	144	144	144	142	144	0.867
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	201	198	213	168	207	197	17.403

Table A39: Young's modulus of LDPE/re-LDPE-CaCO$_3$/LDPE in MD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	Re-LDPE (100)	LDPE (100)	155	162	140	138	145	148	10.355
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	112	124	135	137	136	129	10.561
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	158	155	143	155	140	150	8.028
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	157	150	158	149	150	153	4.135
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	182	191	192	181	195	188	6.238

Table A40: Young's modulus of LDPE/re-LDPE-CaCO$_3$/LDPE in TD

No.	Film formulations (wt%)			Young's modulus (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	Re-LDPE (100)	LDPE (100)	140	128	141	145	145	140	7.137
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	148	146	145	150	142	146	2.871
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	171	157	154	162	159	161	6.433
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	158	153	153	146	151	152	4.316
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	190	184	189	159	185	181	12.722

<div align="center">**Table A41**: Haze of LDPE/LDPE-re-LDPE/LDPE</div>

No.	Film formulations (wt%)			Haze (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	15.70	15.90	16.29	16.00	15.60	15.90	0.270
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	15.70	16.90	13.00	15.50	13.00	14.82	1.746
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	14.80	14.40	14.40	14.50	14.00	14.42	0.286
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	14.20	14.20	14.70	14.00	14.20	14.26	0.261
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	12.60	12.40	12.30	12.50	12.60	12.48	0.130
6	LDPE (100)	re-LDPE (100)	LDPE (100)	13.60	13.50	13.30	13.40	13.60	13.48	0.130

Table A42: Haze of LDPE/re-LDPE-MDPE/LDPE

No.	Film formulations (wt%)			Haze (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	13.60	13.50	13.30	13.40	13.60	13.48	0.130
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	17.50	17.90	15.40	17.90	17.29	17.20	1.039
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	18.40	18.20	18.60	18.70	18.79	18.54	0.238
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	21.30	21.10	20.29	20.60	20.40	20.74	0.442
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	20.60	23.00	20.50	20.90	21.90	21.38	1.062

Table A43: Haze of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE

| No. | Film formulations (wt%) | | | Haze (%) | | | | | | |
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	18.40	18.20	18.60	18.70	18.79	18.54	0.238
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	9.33	9.16	9.18	8.85	9.42	9.19	0.217
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	7.17	6.83	6.48	6.89	6.68	6.81	0.256
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	4.23	4.25	3.67	3.76	4.34	4.05	0.310
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	2.68	2.65	2.74	2.52	2.54	2.63	0.094

Table A44: Haze of LDPE/re-LDPE-CaCO$_3$/LDPE

No.	Film formulations (wt%)			Haze (%)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	Re-LDPE (100)	LDPE (100)	13.60	13.50	13.30	13.40	13.60	13.48	0.130
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	56.50	56.70	56.60	57.60	56.90	56.86	0.439
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	62.90	62.90	64.30	64.40	62.60	63.42	0.858
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	72.80	73.00	71.69	72.40	71.90	72.36	0.562
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	79.40	80.30	78.80	79.50	79.30	79.46	0.541

Table A45: Gloss of LDPE/LDPE-re-LDPE/LDPE

No.	Film formulations (wt%)			Gloss (GU)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	LDPE (100)	LDPE (100)	71.60	71.80	70.70	71.40	70.90	71.28	0.466
2	LDPE (100)	LDPE : re-LDPE (85:15)	LDPE (100)	69.60	70.60	70.10	70.90	69.90	70.22	0.526
3	LDPE (100)	LDPE : re-LDPE (70:30)	LDPE (100)	69.70	69.70	69.80	69.90	70.50	69.92	0.335
4	LDPE (100)	LDPE : re-LDPE (55:45)	LDPE (100)	70.20	70.80	69.10	69.60	69.40	69.82	0.680
5	LDPE (100)	LDPE : re-LDPE (40:60)	LDPE (100)	69.60	69.90	69.40	70.90	70.70	70.10	0.667
6	LDPE (100)	re-LDPE (100)	LDPE (100)	67.10	67.30	67.60	67.70	67.40	67.42	0.239

Table A46: Gloss of LDPE/re-LDPE-MDPE/LDPE

No.	Film formulations (wt%)			Gloss (GU)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE (100)	LDPE (100)	67.10	67.30	67.60	67.70	67.40	67.42	0.239
2	LDPE (100)	re-LDPE : MDPE (85:15)	LDPE (100)	68.20	68.30	68.90	69.70	68.70	68.76	0.598
3	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	70.40	70.80	70.90	70.80	70.70	70.72	0.192
4	LDPE (100)	re-LDPE : MDPE (55:45)	LDPE (100)	68.30	66.80	68.30	68.90	69.90	68.44	1.126
5	LDPE (100)	re-LDPE : MDPE (40:60)	LDPE (100)	68.60	68.70	68.20	69.30	70.90	69.14	1.060

Table A47: Gloss of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE

No.	Film formulations (wt%)			Gloss (GU)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	re-LDPE : MDPE (70:30)	LDPE (100)	70.40	70.80	70.90	70.80	70.70	70.72	0.192
2	LDPE : LLDPE (85:15)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (85:15)	75.30	75.90	75.60	75.40	76.10	75.66	0.336
3	LDPE : LLDPE (70:30)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (70:30)	78.40	78.60	78.70	79.20	77.00	78.38	0.826
4	LDPE : LLDPE (55:45)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (55:45)	79.80	80.10	80.60	80.70	80.40	80.32	0.370
5	LDPE : LLDPE (40:60)	re-LDPE : MDPE (70:30)	LDPE : LLDPE (40:60)	83.40	83.30	83.70	83.90	83.80	83.62	0.259

Table A48: Gloss of LDPE/re-LDPE-CaCO$_3$/LDPE

No.	Film formulations (wt%)			Gloss (GU)						
	Outer	Middle	Outer	1	2	3	4	5	X	STD
1	LDPE (100)	Re-LDPE (100)	LDPE (100)	67.10	67.30	67.60	67.70	67.40	67.42	0.239
2	LDPE (100)	re-LDPE : CaCO$_3$ (95:5)	LDPE (100)	50.40	50.80	50.60	51.20	50.90	50.78	0.303
3	LDPE (100)	re-LDPE : CaCO$_3$ (92.5:7.5)	LDPE (100)	50.00	49.50	50.40	50.20	49.40	49.90	0.436
4	LDPE (100)	re-LDPE : CaCO$_3$ (90:10)	LDPE (100)	50.40	50.30	50.40	50.20	50.10	50.28	0.130
5	LDPE (100)	re-LDPE : CaCO$_3$ (85:15)	LDPE (100)	50.50	50.70	50.80	51.20	51.30	50.90	0.339

APPENDIX B
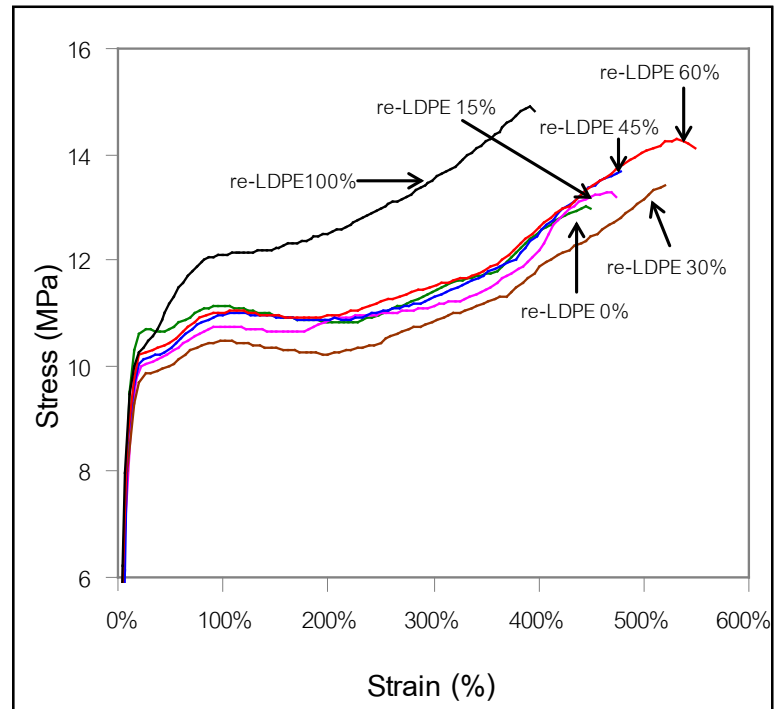
Figure B-1 Stress-strain curves of LDPE/LDPE-re-LDPE/LDPE in MD
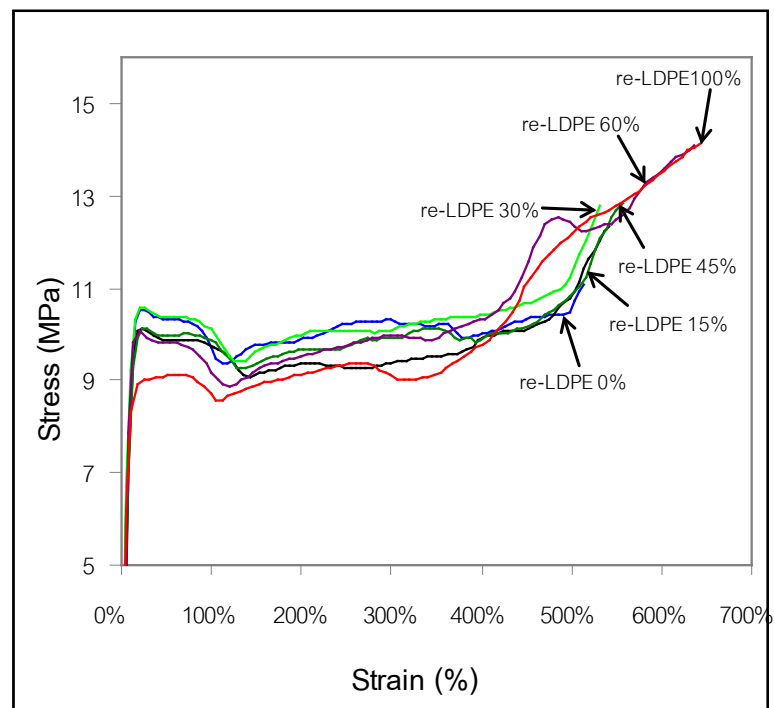
Figure B-2 Stress-strain curves of LDPE/LDPE-re-LDPE/LDPE in TD
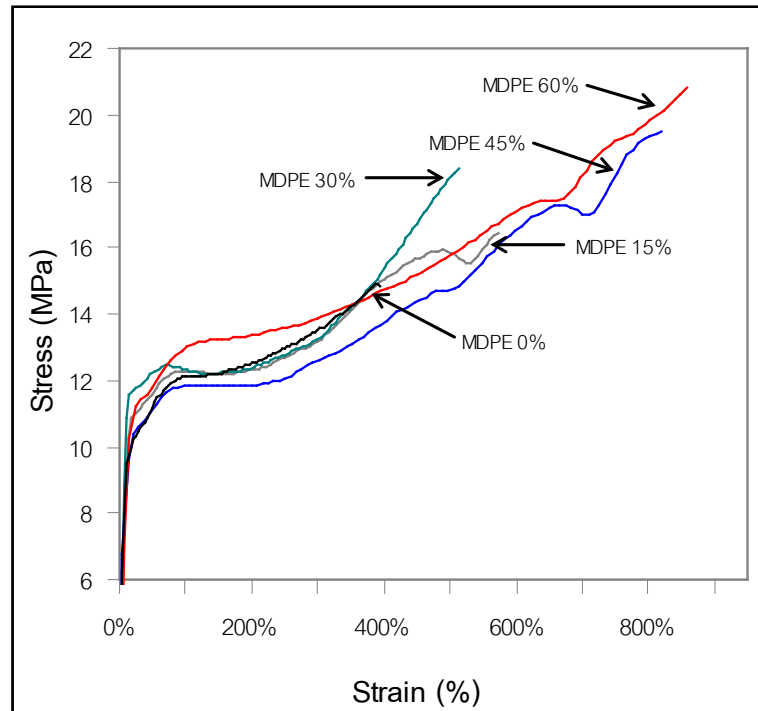
Figure B-3 Stress-strain curves of LDPE/re-LDPE-MDPE/LDPE in MD
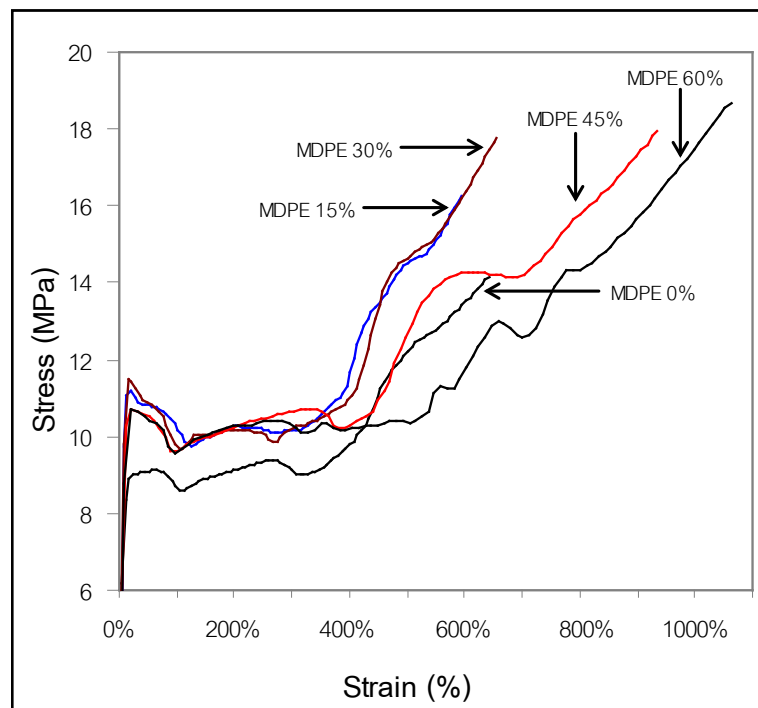
Figure B-4 Stress-strain curves of LDPE/re-LDPE-MDPE/LDPE in TD
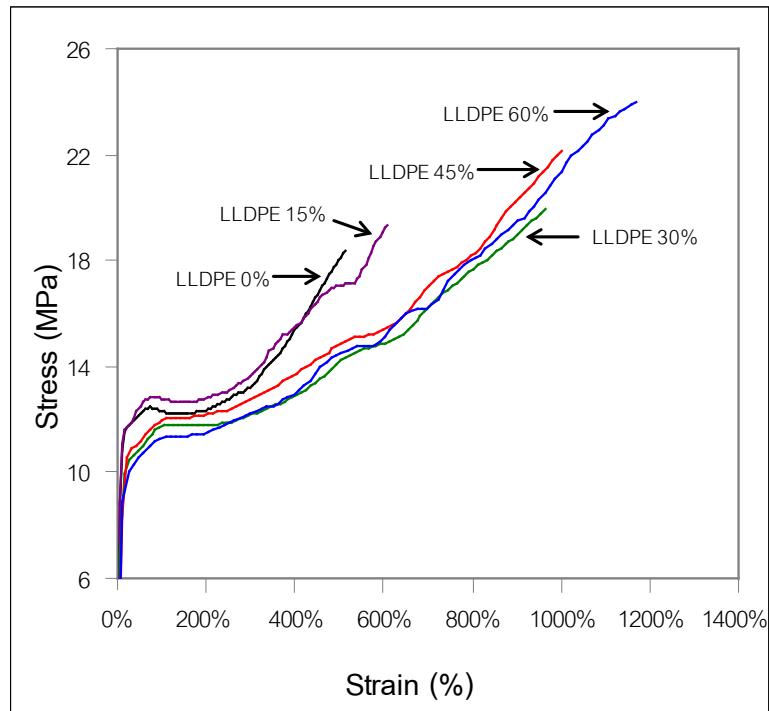
Figure B-5 Stress-strain curves of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD
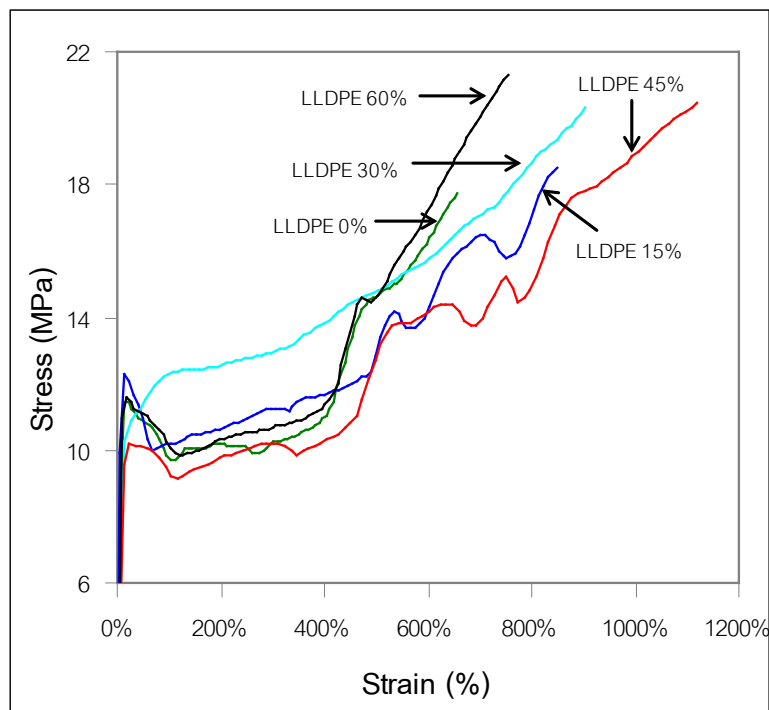
Figure B-6 Stress-strain curves of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in TD
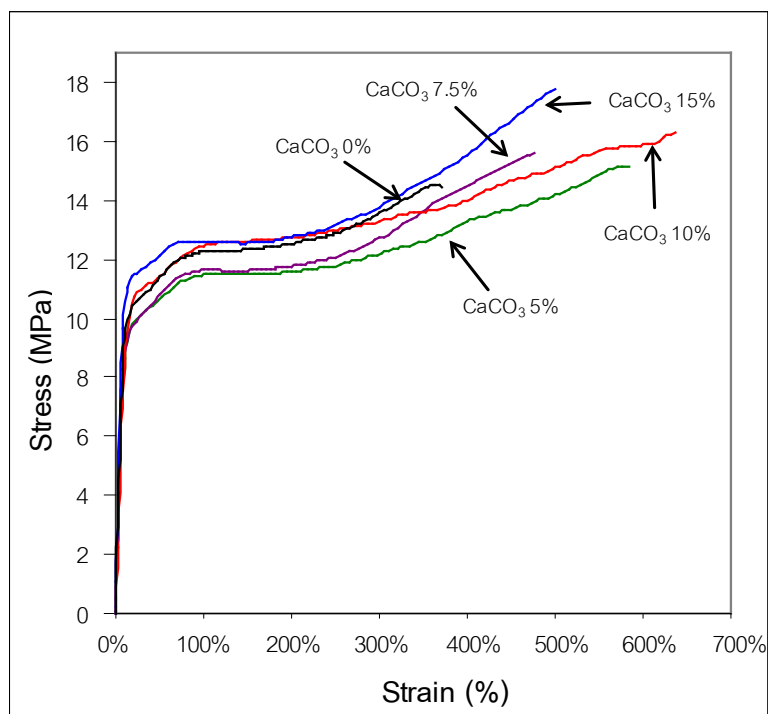
Figure B-7 Stress-strain curves of LDPE/re-LDPE-CaCO$_3$/LDPE in MD
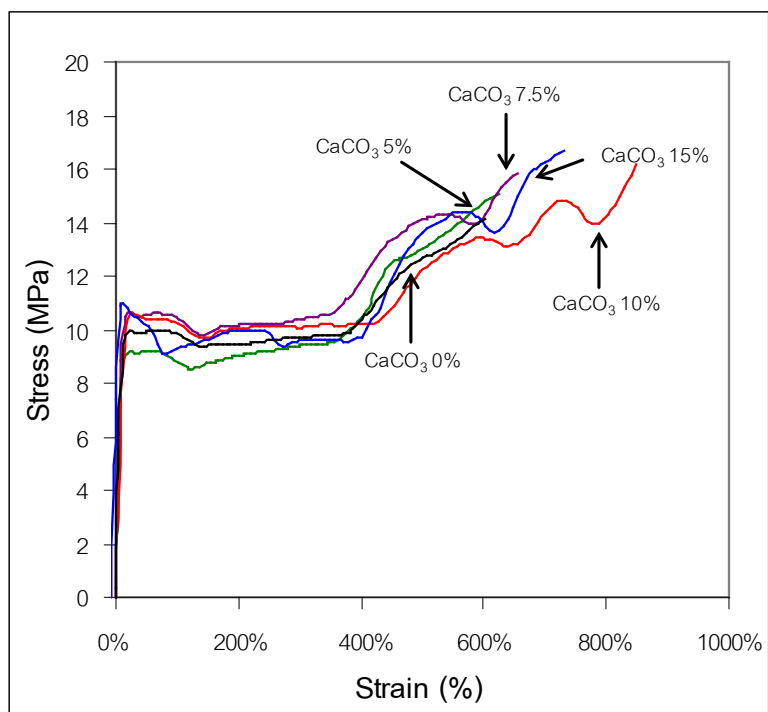
Figure B-8 Stress-strain curves of LDPE/re-LDPE-CaCO$_3$/LDPE in TD
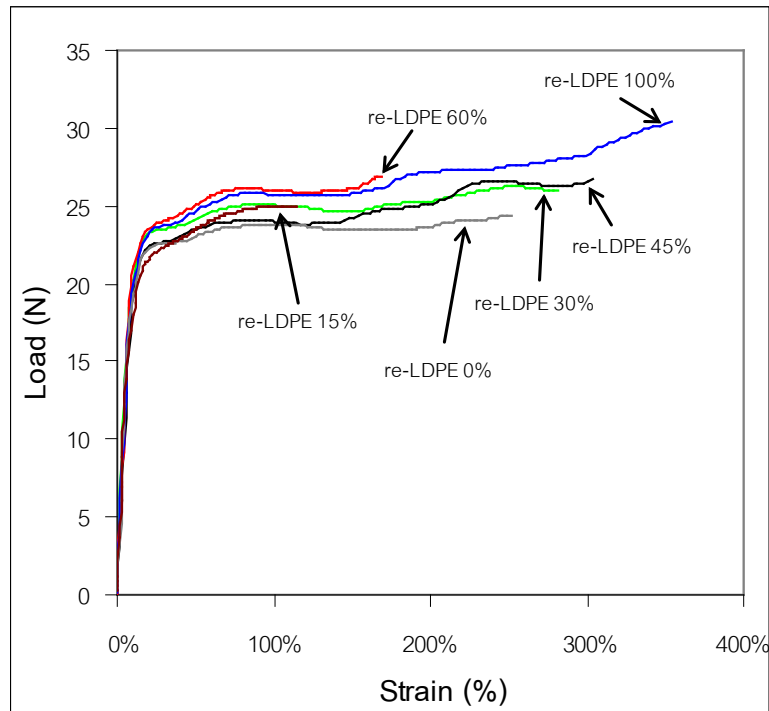
Figure B-9 Seal strength curves of LDPE/LDPE-re-LDPE/LDPE in MD
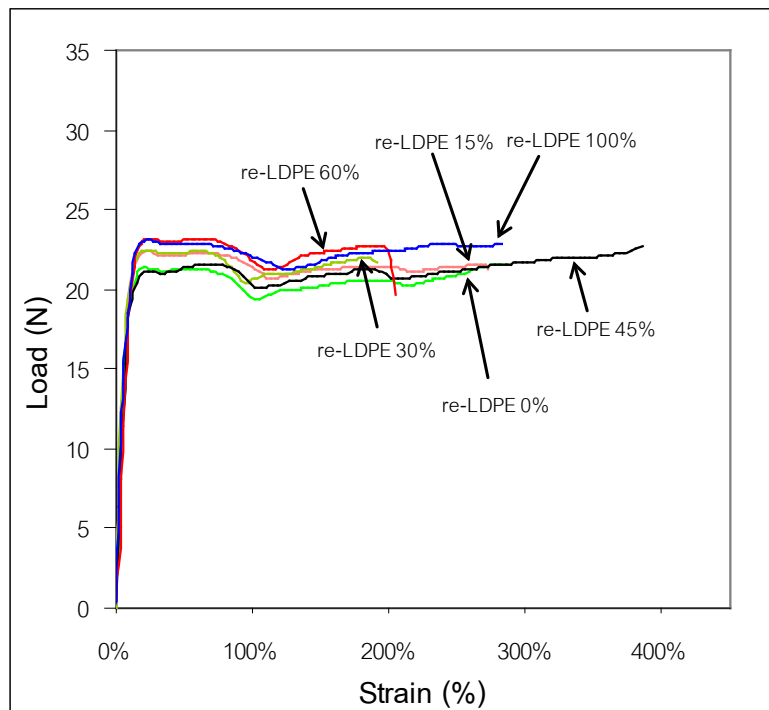
Figure B-10 Seal strength curves of LDPE/LDPE-re-LDPE/LDPE in TD
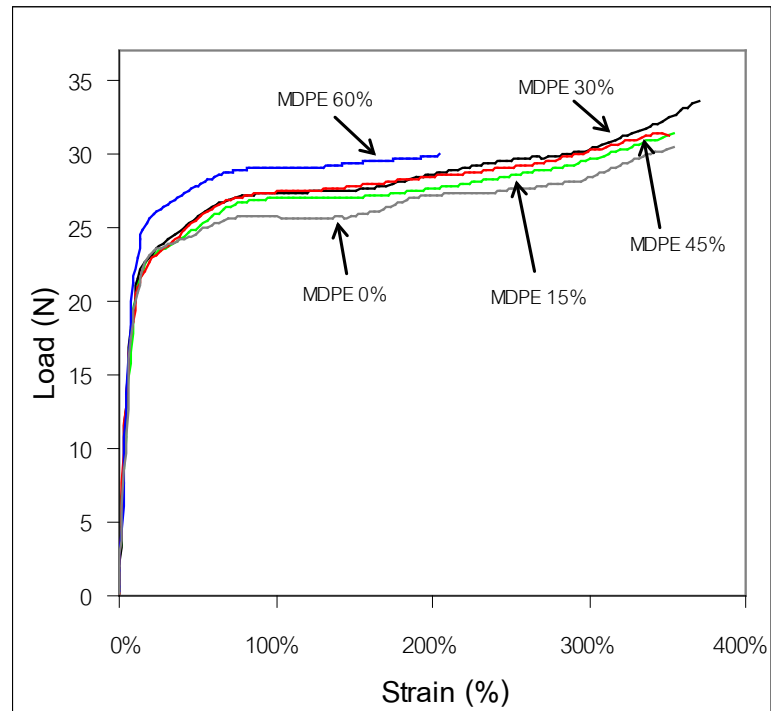
Figure B-11 Seal strength curves of LDPE/re-LDPE-MDPE/LDPE in MD
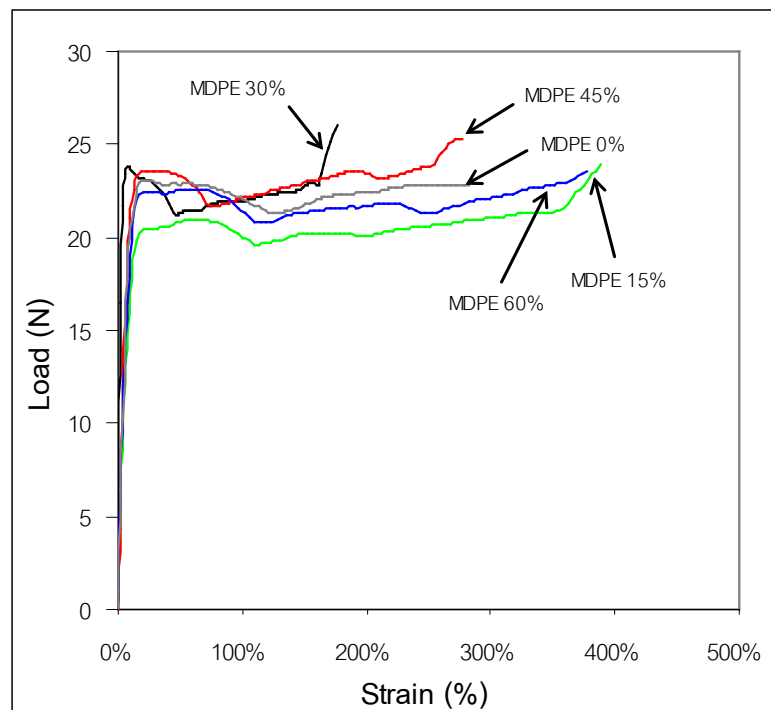
Figure B-12 Seal strength curves of LDPE/re-LDPE-MDPE/LDPE in TD
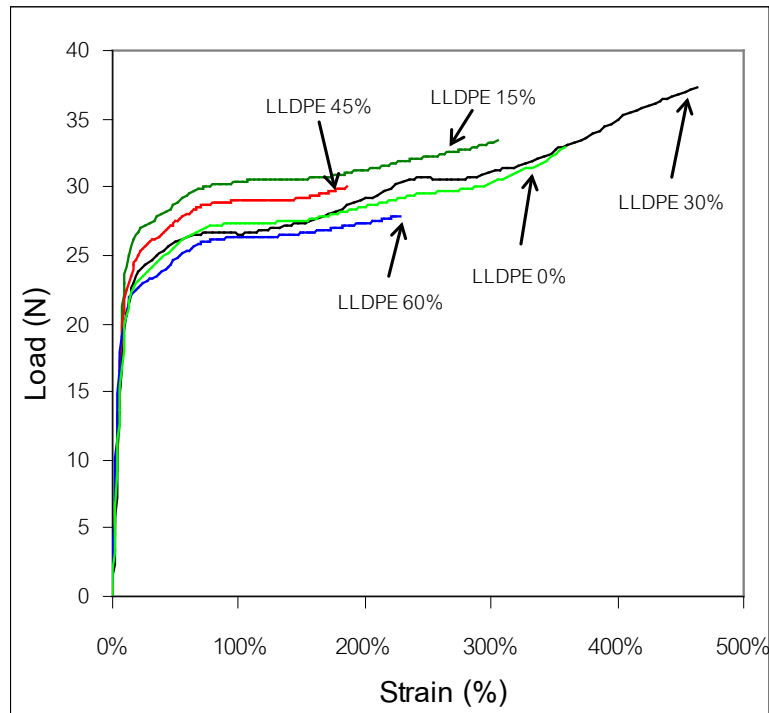
Figure B-13 Seal strength curves of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in MD
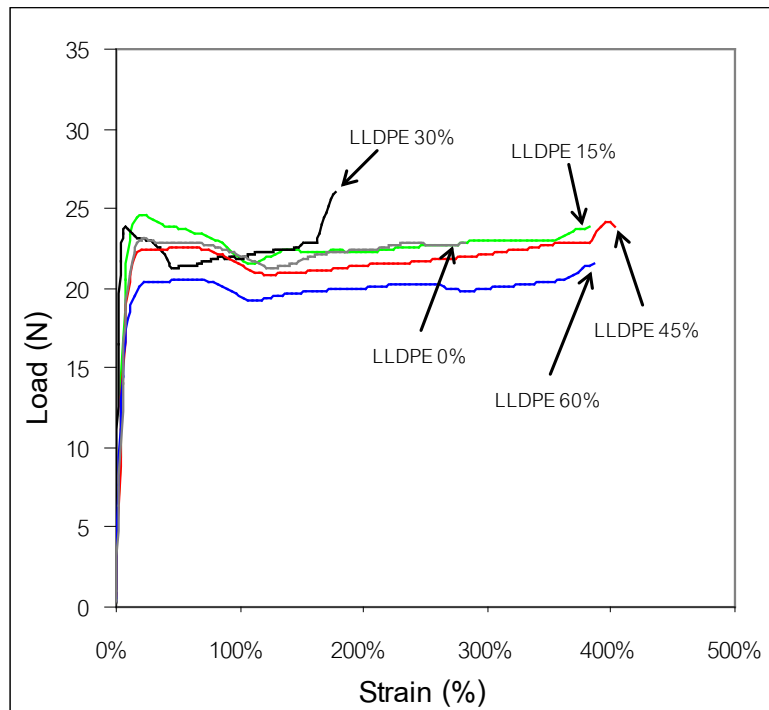
Figure B-14 Seal strength curves of LDPE-LLDPE/re-LDPE-MDPE/LDPE-LLDPE in TD
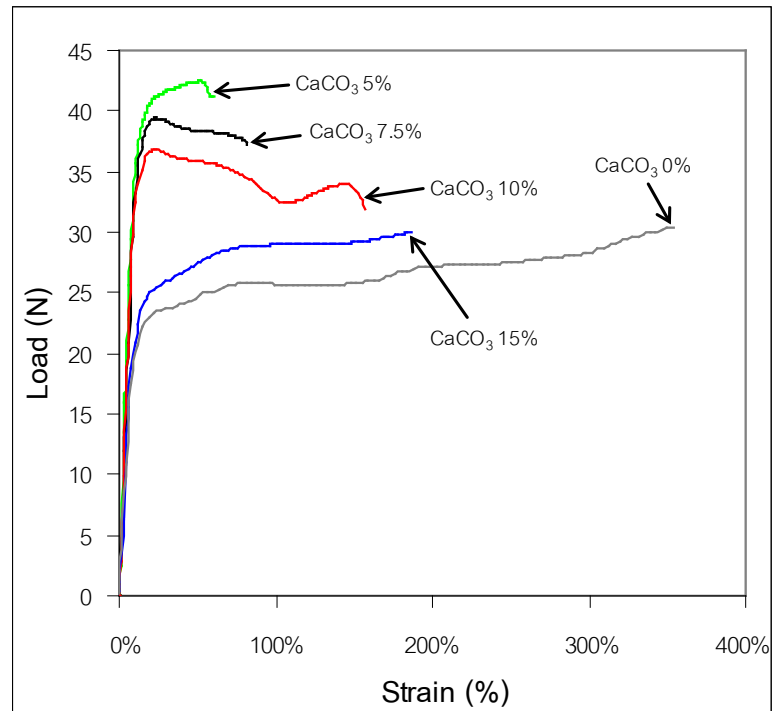
Figure B-15 Seal strength curves of LDPE/re-LDPE-CaCO$_3$/LDPE in MD
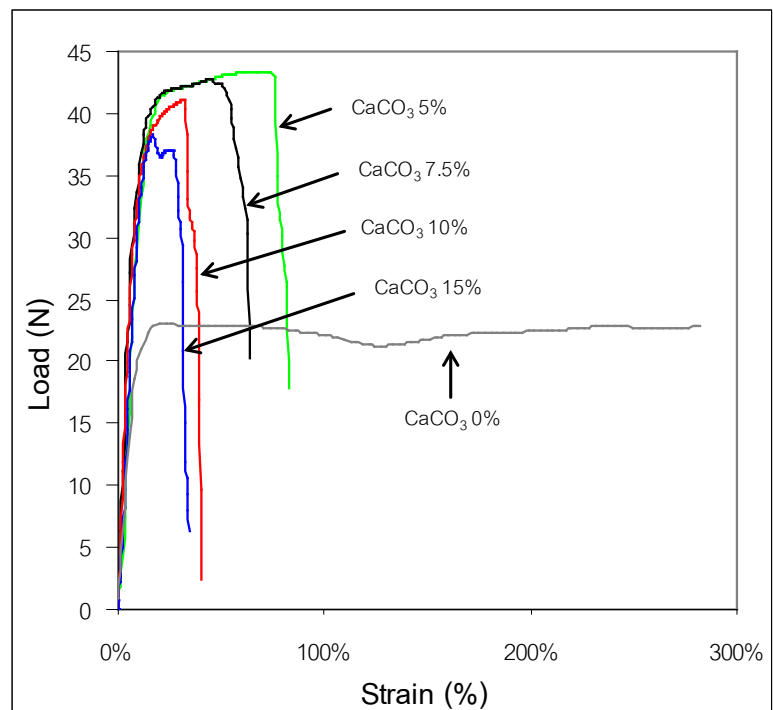
Figure B-16 Seal strength curves of LDPE/re-LDPE-CaCO$_3$/LDPE in TD
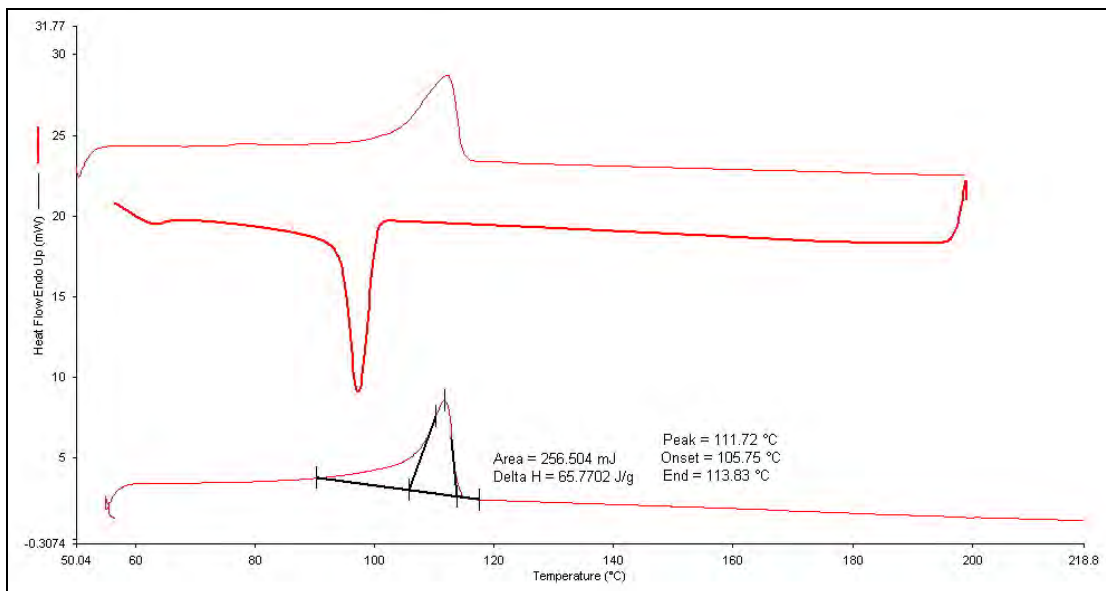
Figure B-17 DSC thermogram of LDPE resin
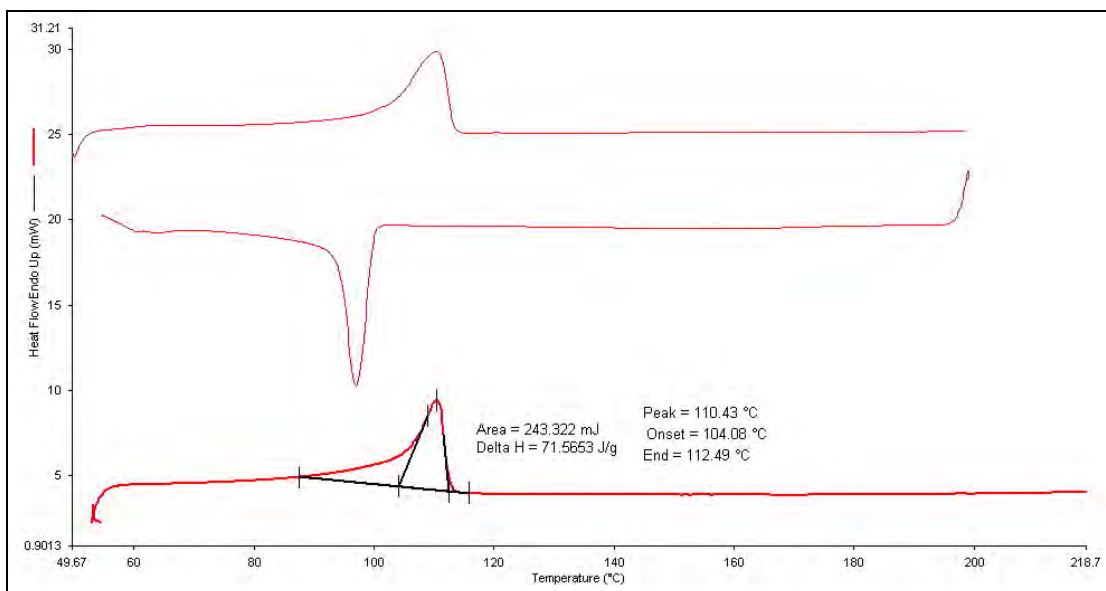
Figure B-18 DSC thermogram of re-LDPE resin
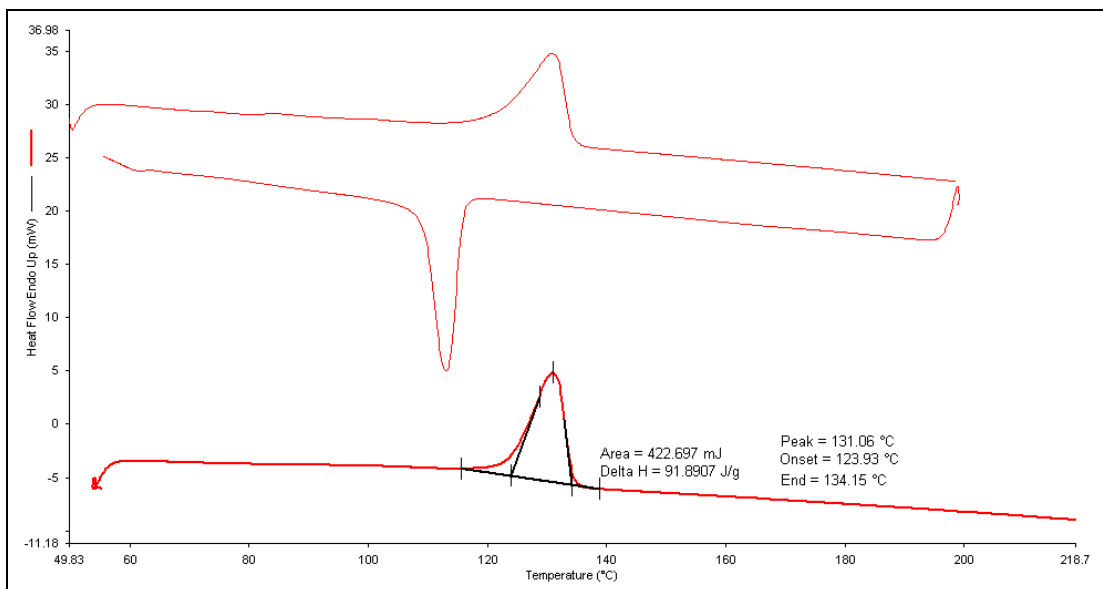
Figure B-19 DSC thermogram of MDPE resin
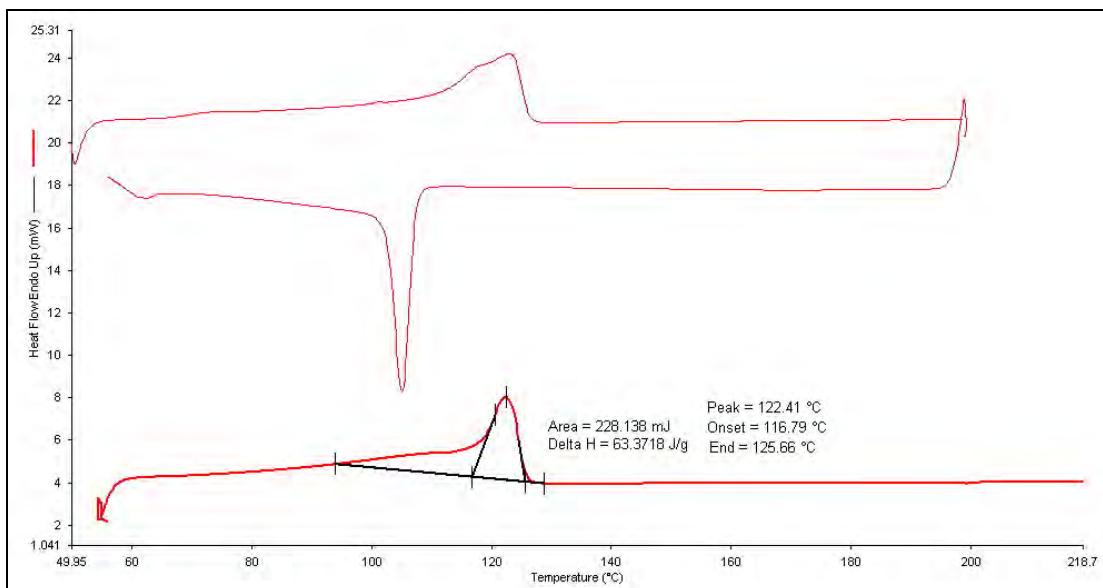
Figure B-20 DSC thermogram of LLDPE resin
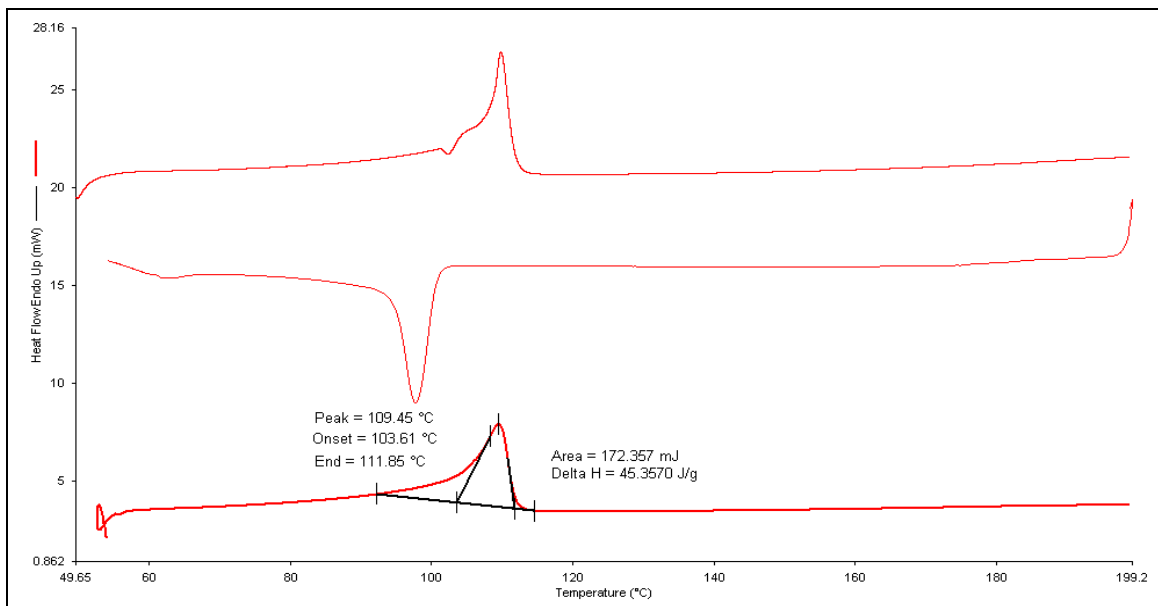
Figure B-21 DSC thermogram of LDPE/LDPE/LDPE
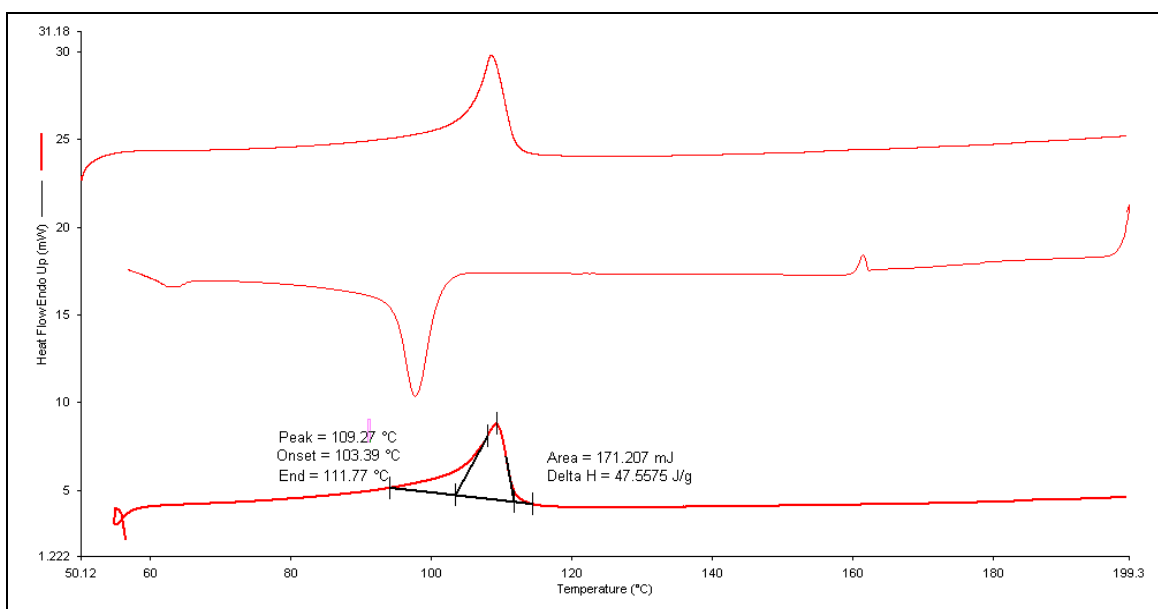
Figure B-22 DSC thermogram of LDPE/LDPE-re-LDPE(85:15)/LDPE
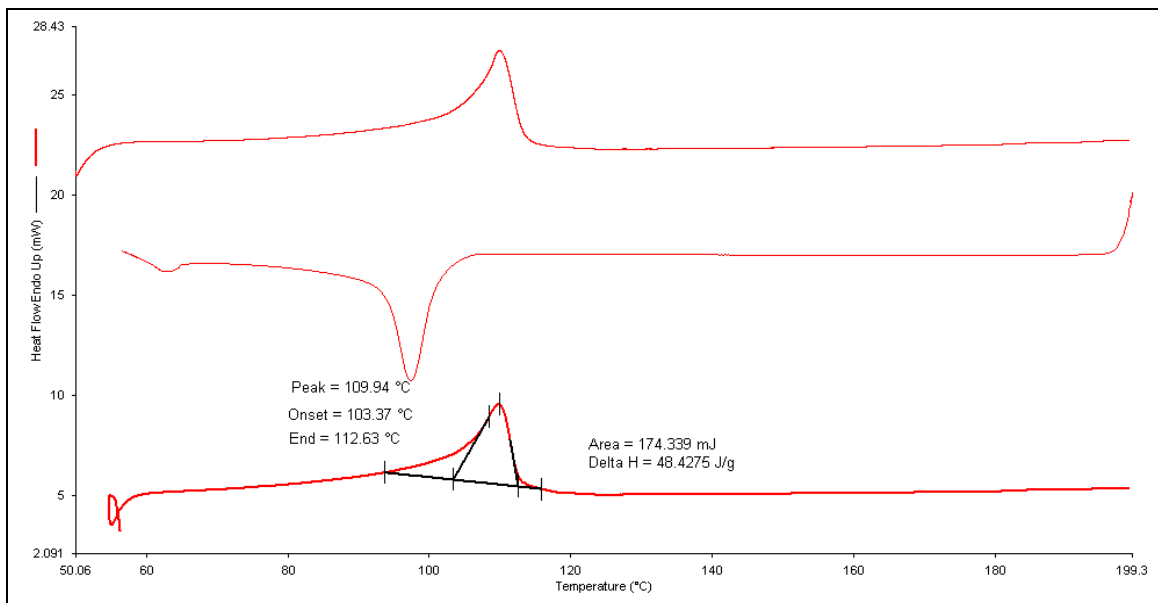
Figure B-23 DSC thermogram of LDPE/LDPE-re-LDPE(70:30)/LDPE
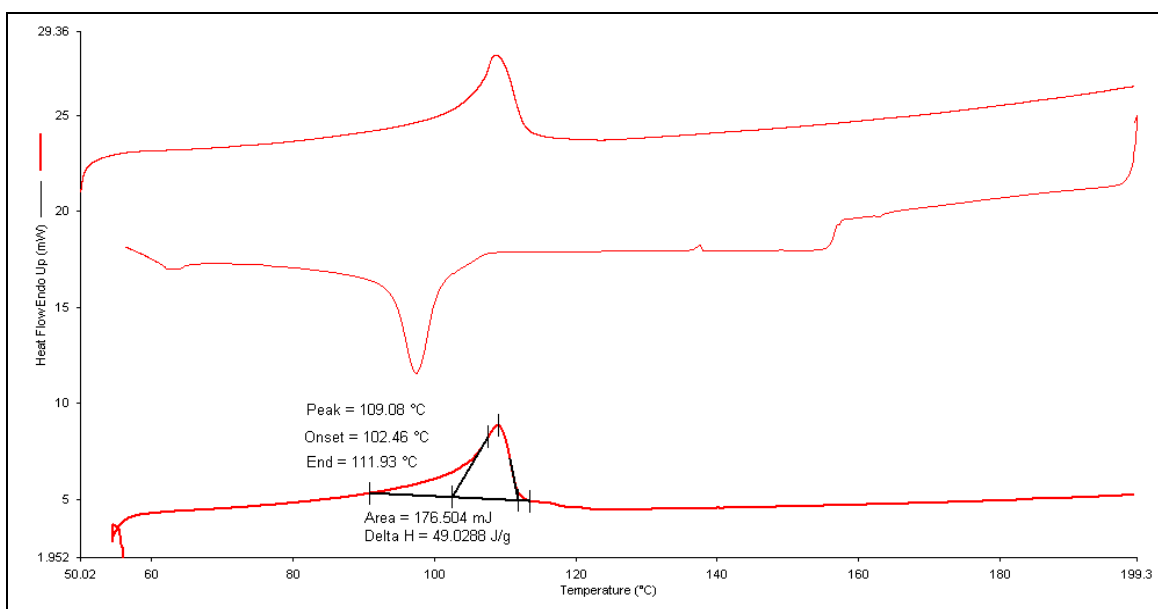
Figure B-24 DSC thermogram of LDPE/LDPE-re-LDPE(55:45)/LDPE
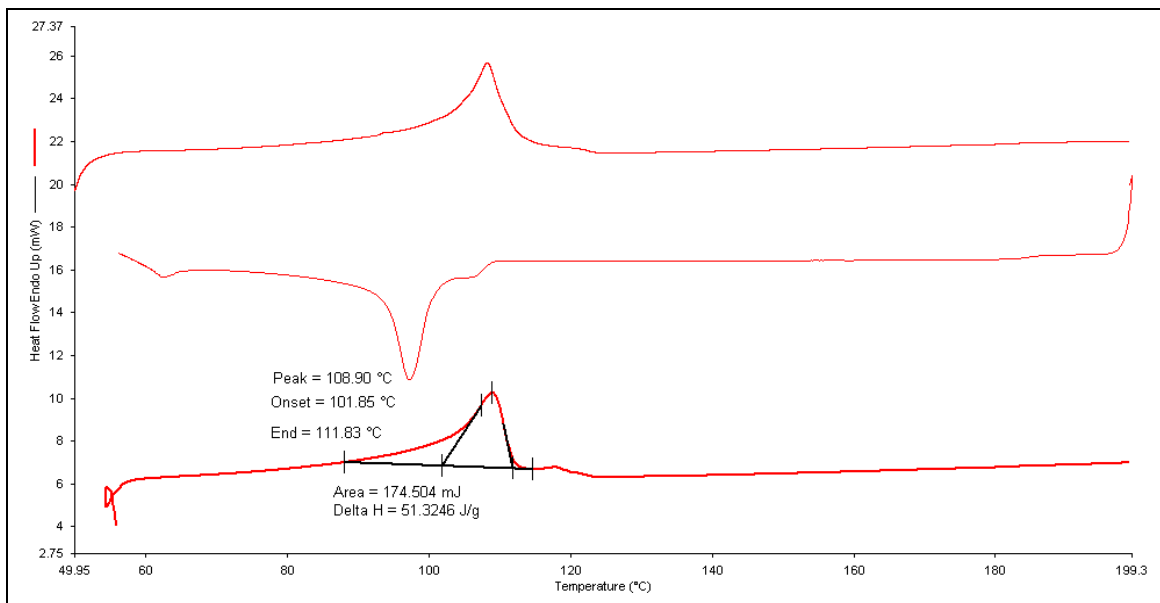
Figure B-25 DSC thermogram of LDPE/LDPE-re-LDPE(40:60)/LDPE
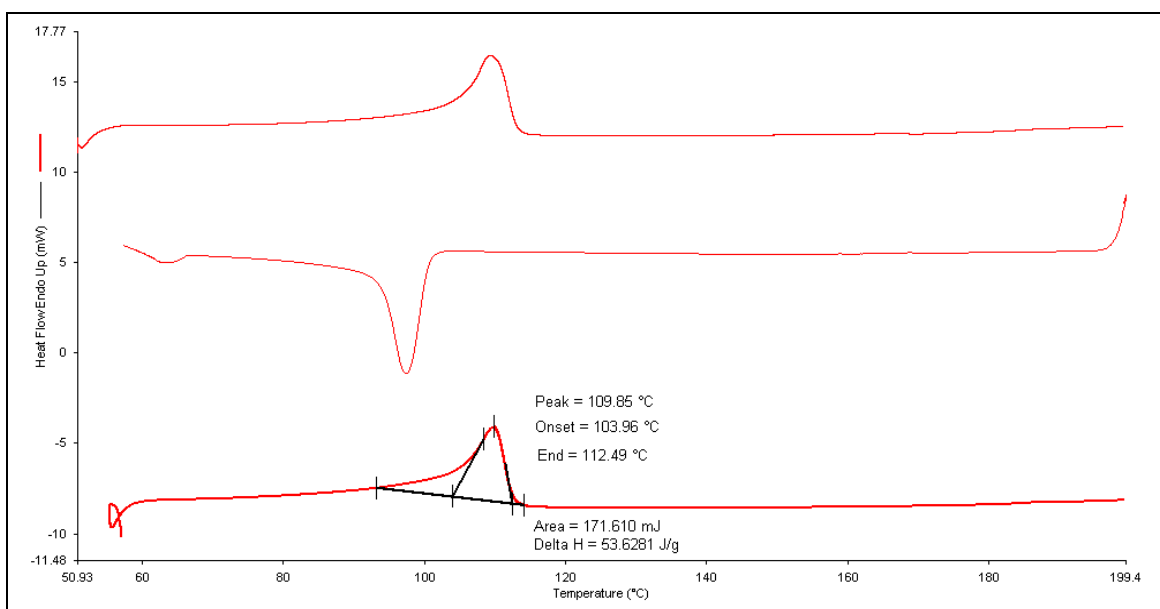
Figure B-26 DSC thermogram of LDPE/re-LDPE /LDPE
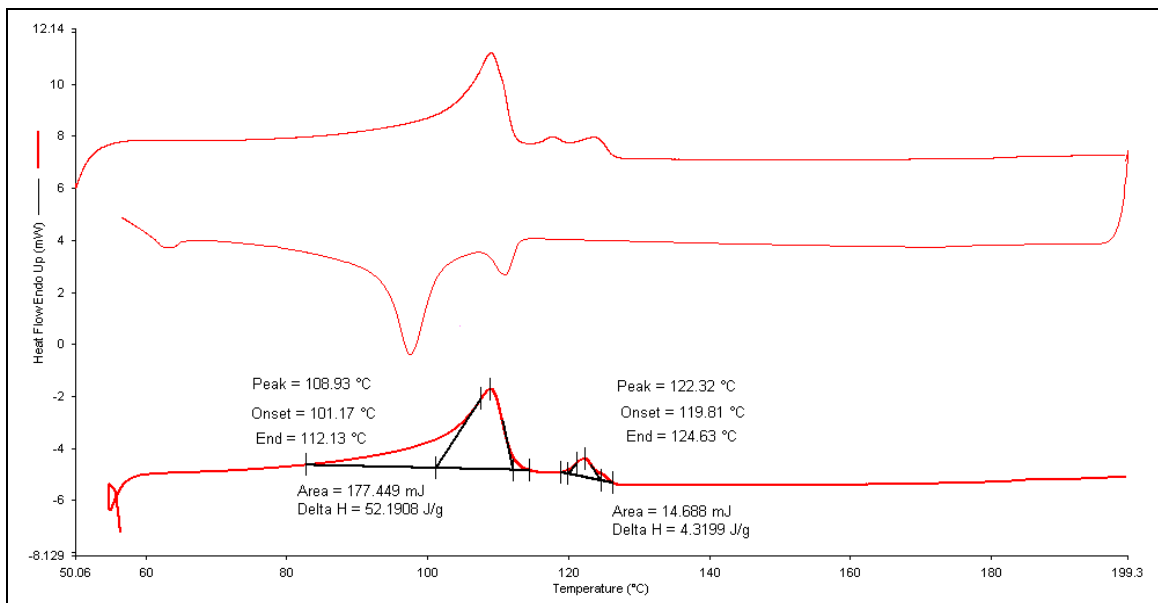
Figure B-27 DSC thermogram of LDPE/re-LDPE-MDPE(85:15)/LDPE
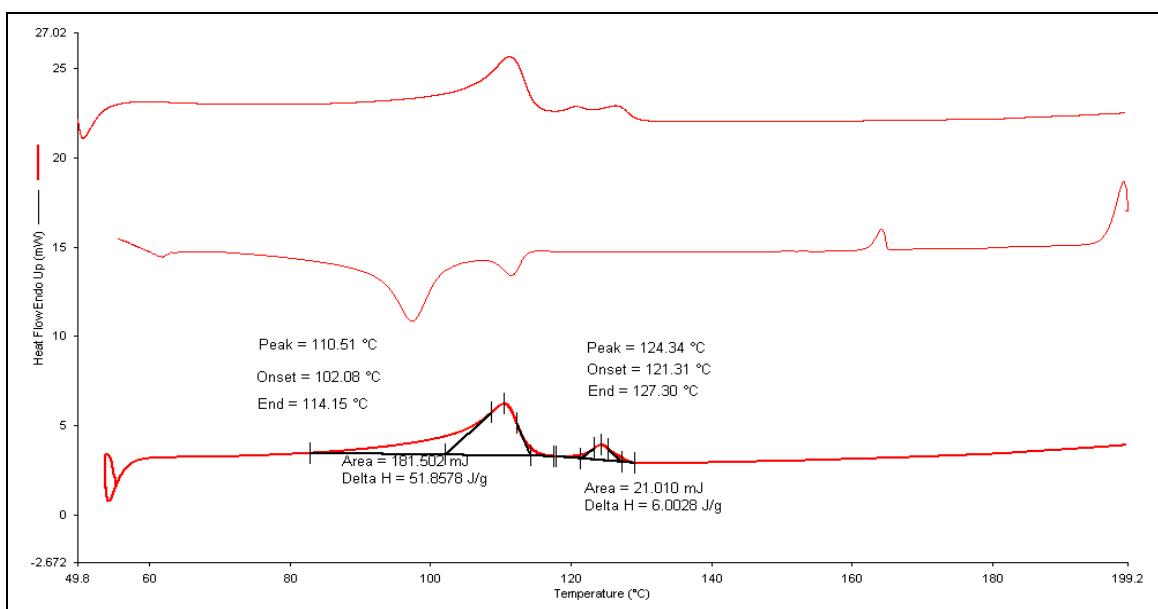
Figure B-28 DSC thermogram of LDPE/re-LDPE-MDPE(70:30)/LDPE
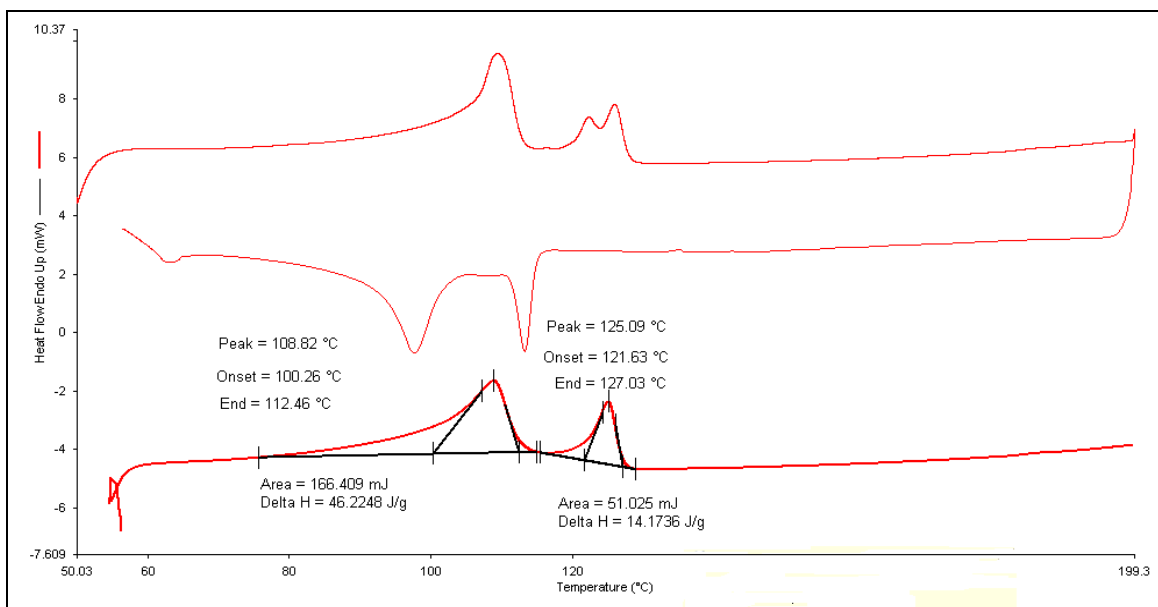
Figure B-29 DSC thermogram of LDPE/re-LDPE-MDPE(55:45)/LDPE
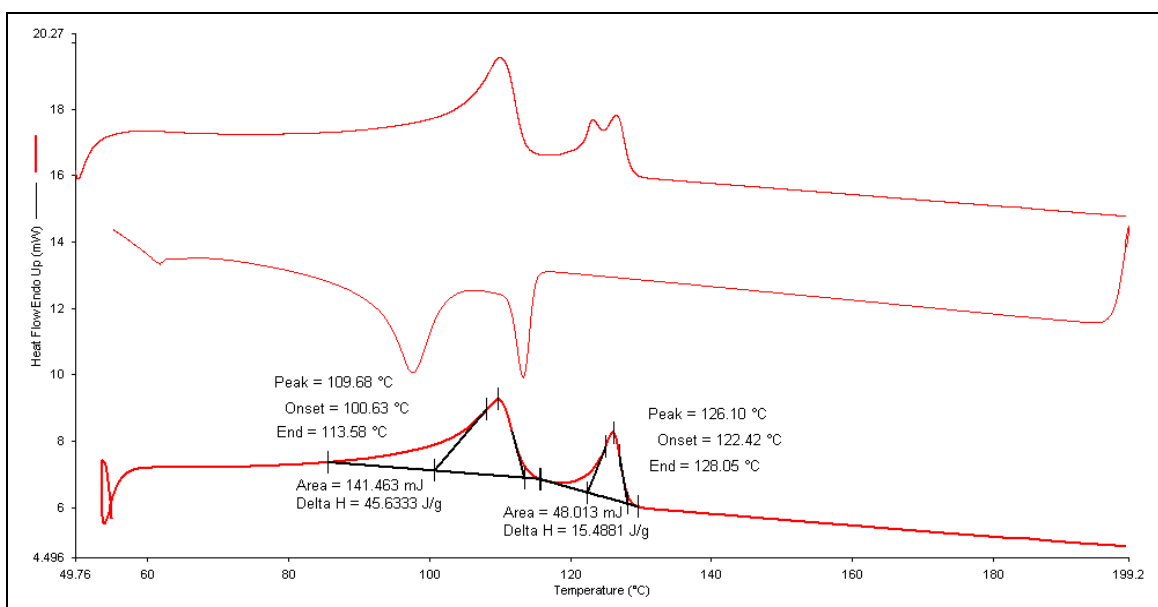
Figure B-30 DSC thermogram of LDPE/re-LDPE-MDPE(40:60)/LDPE
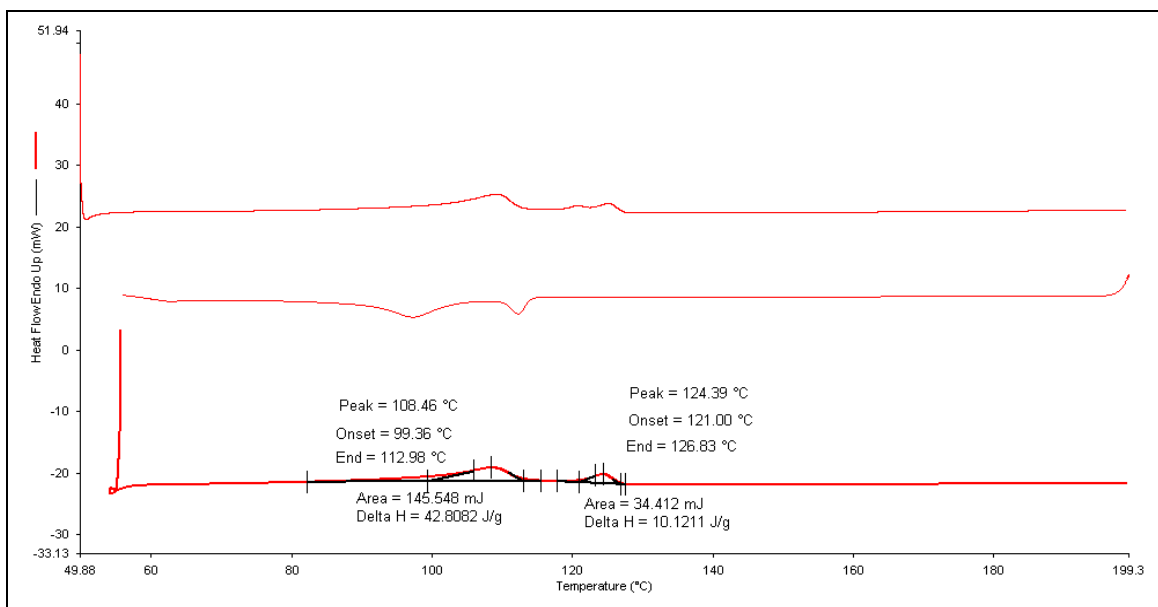
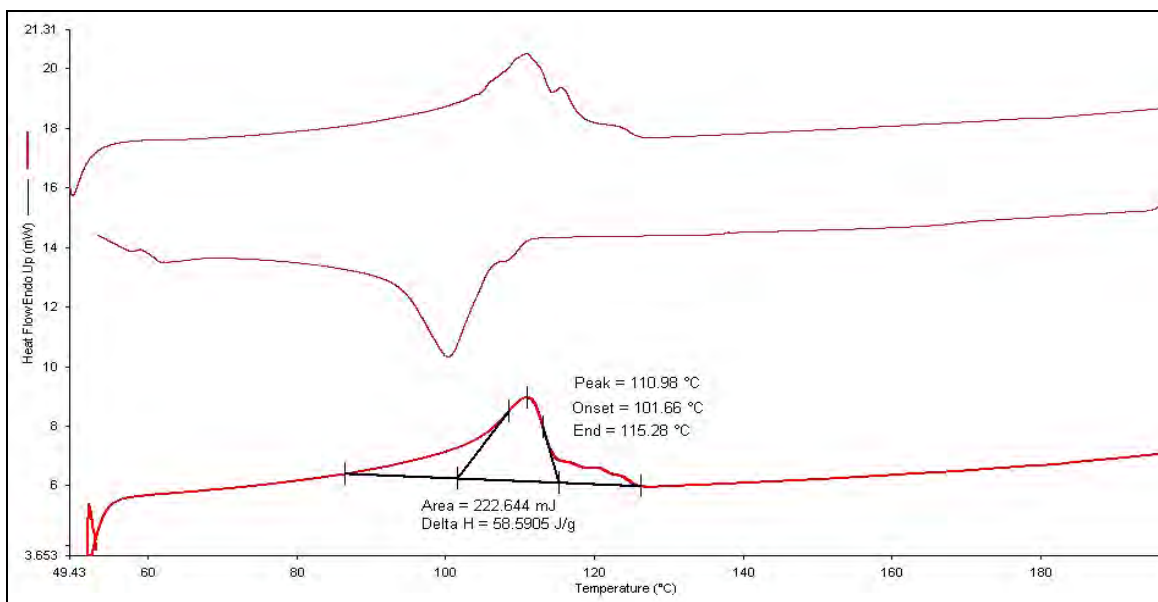Figure B-31 DSC thermogram of LDPE-LLDPE(85:15)/re-DPE-MDPE(70:30)/LDPE-

LLDPE(85:15)
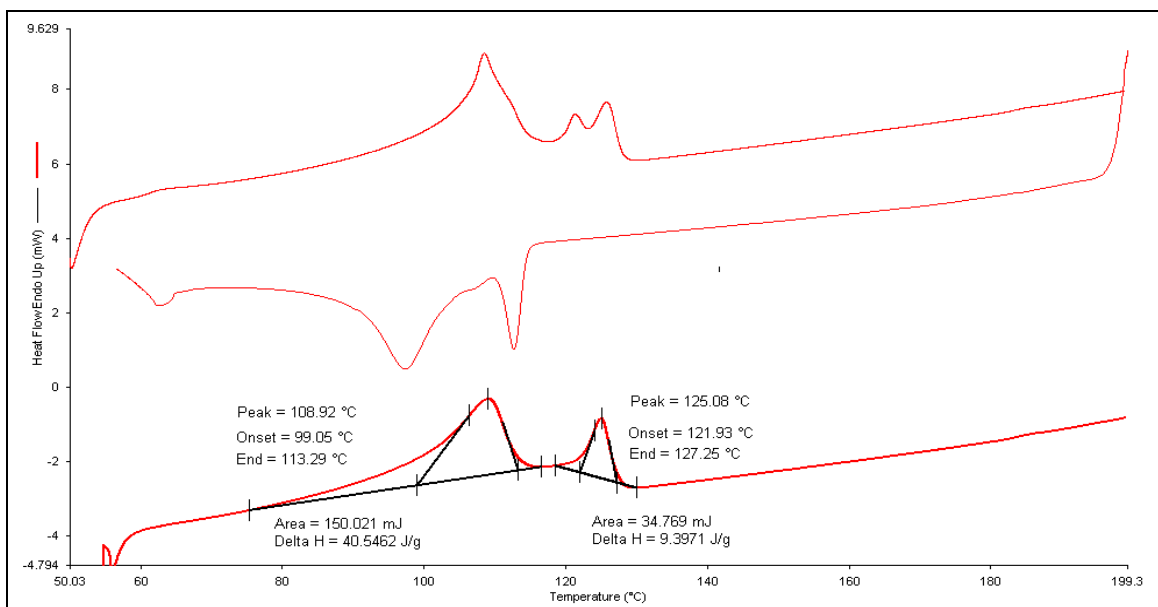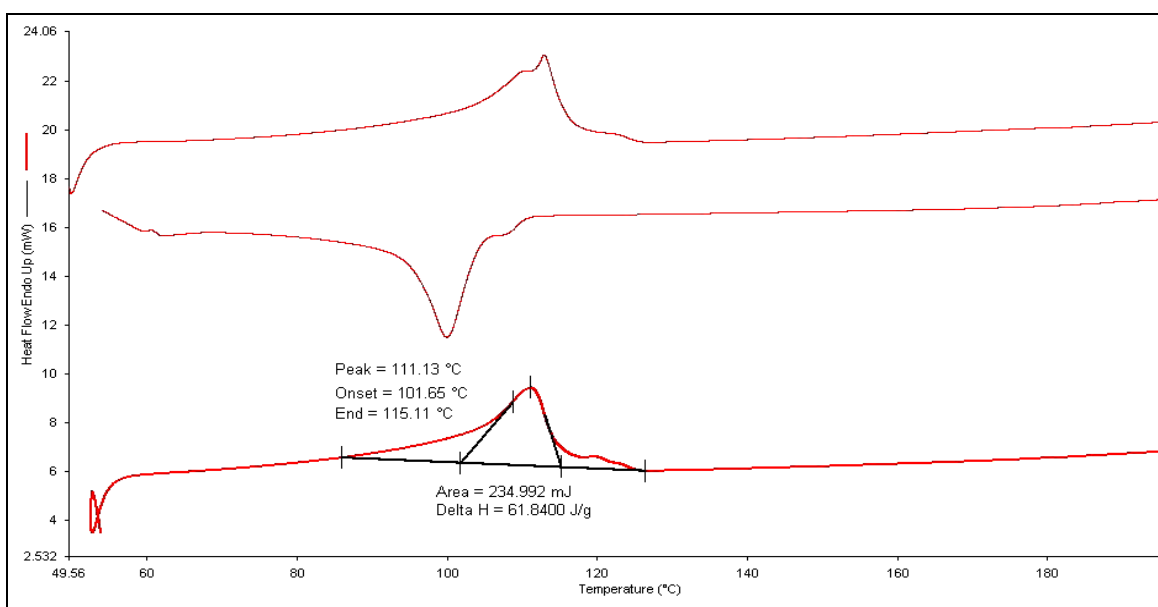

Figure B-32 DSC thermogram of LDPE-LLDPE(70:30)/re-DPE-MDPE(70:30)/LDPE-
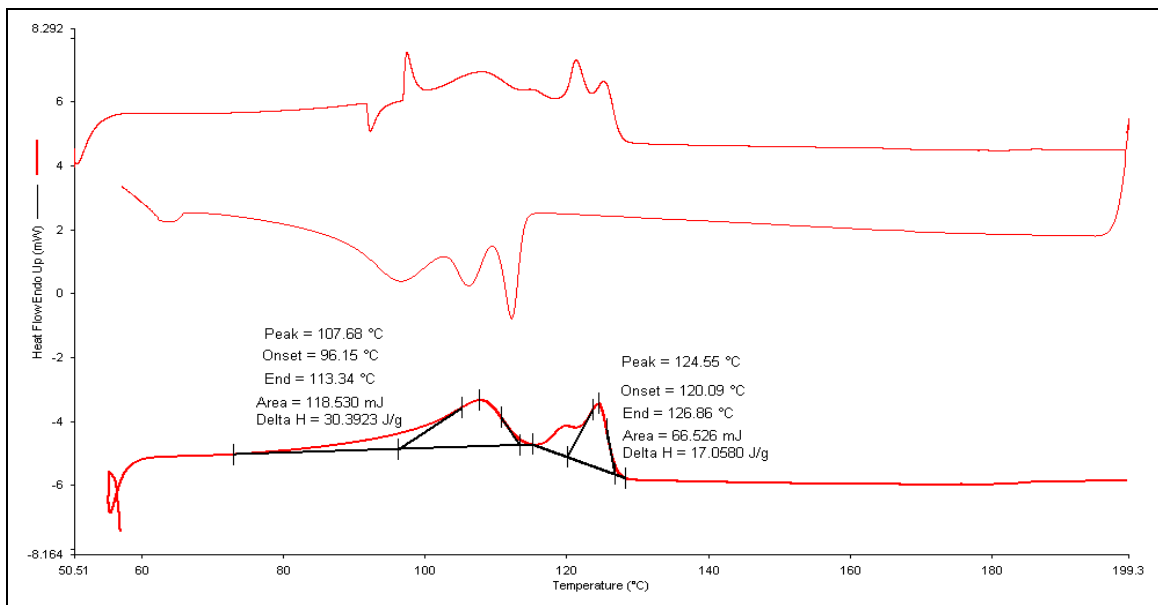
LLDPE(70:30)

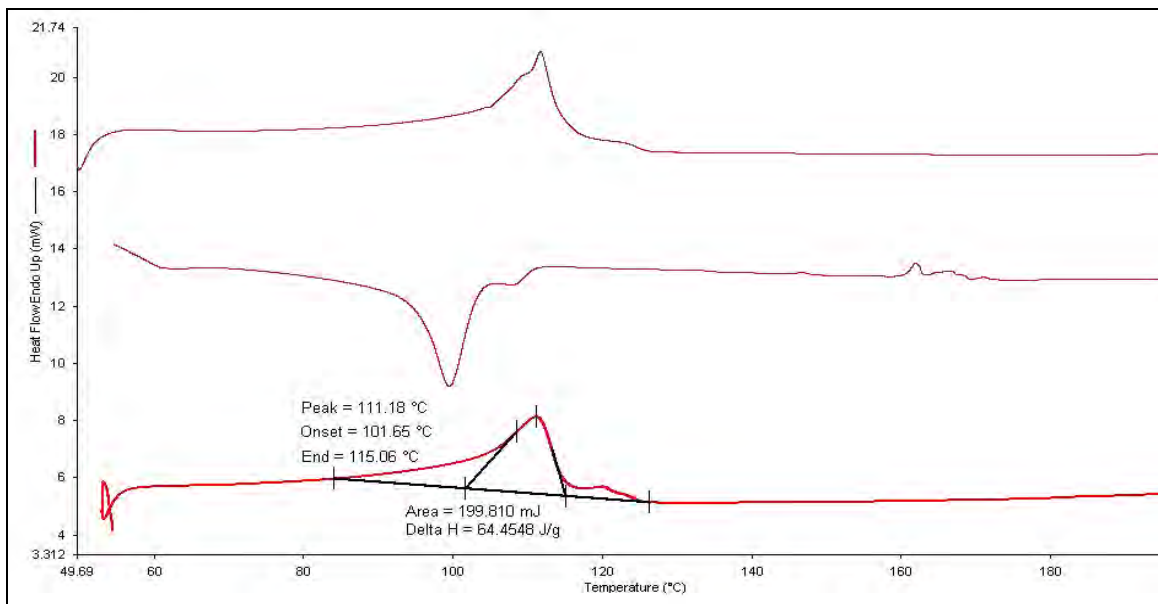Figure B-33 DSC thermogram of LDPE-LLDPE(55:45)/re-DPE-MDPE(70:30)/LDPE-
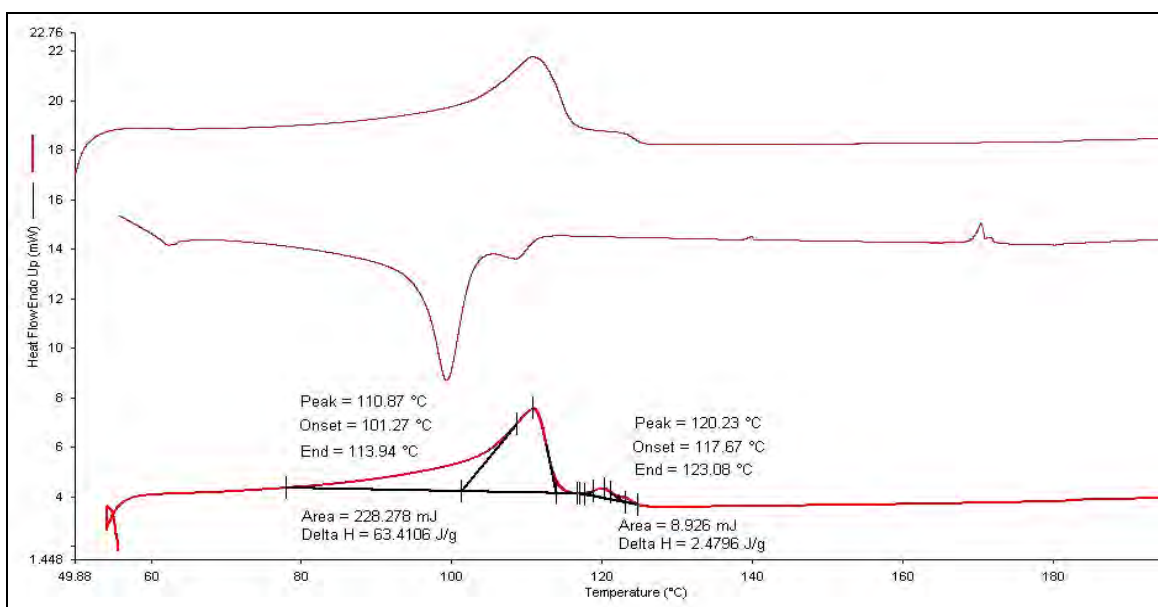
LLDPE(55:45)
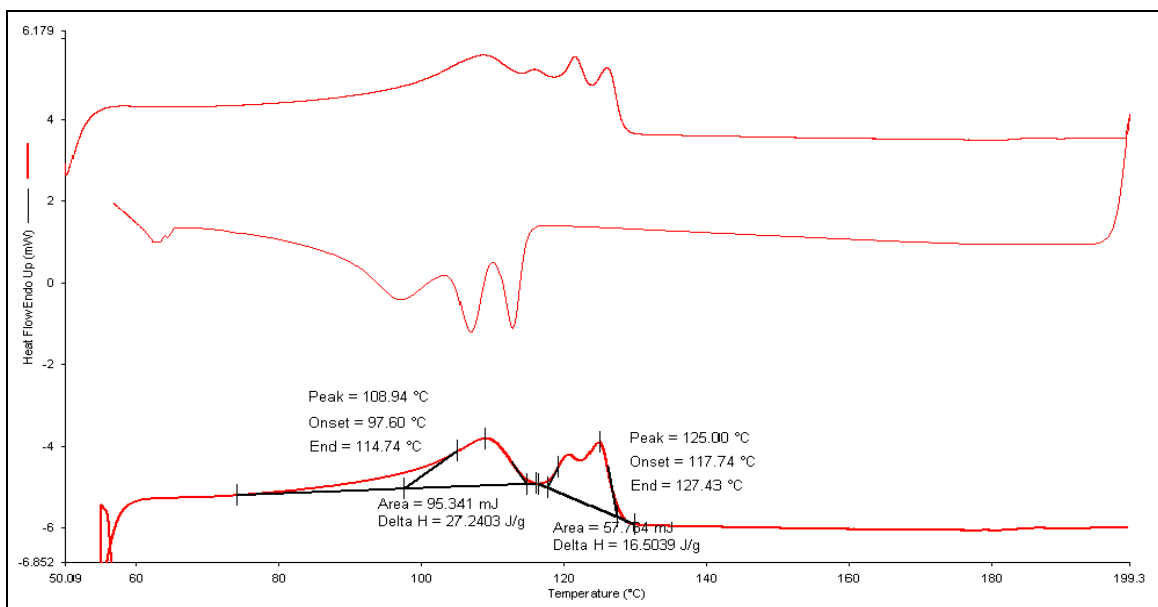
Figure B-34 DSC thermogram of LDPE-LLDPE(40:60)/re-DPE-MDPE(70:30)/LDPE-

LLDPE(40:60)

Figure B-35 DSC thermogram of LDPE/re-LDPE-CaCO$_3$(95:5)/LDPE

Figure B-36 DSC thermogram of LDPE/re-LDPE-CaCO$_3$(92.5:7.5)/LDPE

Figure B-37 DSC thermogram of LDPE/re-LDPE-CaCO$_3$(90:10)/LDPE

Figure B-38 DSC thermogram of LDPE/re-LDPE-CaCO$_3$(85:15)/LDPE

BIOGRAPHY

Miss Omattaya Montrikul was born in Saraburi, Thailand, on October 24th, 1978. She received a Bechelor of Engineering with a major in Polymer Engineering from Suranaree University of Technology, Thailand, in 2001. And she graduated a Master of Engineering with a major in Materials Engineering from King Mongkut's University of Technology Thonburi, Thailand, in 2004. She started as a graduate student in the field of Materials Science, Department of Materials Science, Chulalongkorn University in 2005 and completed the program in 2009.